LINKING CARBON, NITROGEN, AND CALCIUM CYCLING IN NORTHEASTERN U.S. FORESTS

A Dissertation

Presented to the Faculty of the Graduate School

of Cornell University

In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

by

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January 2012

LINKING CARBON, NITROGEN, AND CALCIUM CYCLING IN NORTHEASTERN U.S. FORESTS

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Cornell University 2012

Carbon (C), nitrogen (N), and calcium (Ca) cycling in forest ecosystems is controlled largely by the recycling of organic matter by biota and by the balance of new inputs and losses. In the northeastern U.S., the availability of these elements has been dramatically altered by human activities. Acid deposition has increased N inputs and caused declines in soil Ca concentrations. Concurrently, atmospheric carbon dioxide concentrations are rising. My dissertation research focused on understanding how individual tree species influence ecosystem C, N, and Ca cycling, and how increasing soil Ca by liming affects C and N pools, fluxes, and dissolved organic matter retention.

In chapter 1, I show how Norway spruce, red oak, and sugar maple planted in a common garden influence soil C, N, and Ca pools. Norway spruce had the largest C and N stocks in the forest floor and upper mineral soils. No differences among species were observed in soil exchangeable Ca availability. Red oak plots displayed the highest foliar litter lignin concentrations, the shortest residence time for C and N in the forest floor, and the highest earthworm densities. This suggests that leaf litter recalcitrance is not the dominant driver of decomposition in this forest and that other factors, such as the presence of earthworms, can influence organic matter turnover in ways that are unexpected when only considering litter chemistry.

In chapters 2 and 3, I discuss the long-term effects of liming on ecosystem C and N dynamics. Twenty years after lime addition, there was no evidence of a tree response. Within the forest floor, C and N stocks in limed soils were double that found in controls. I observed reductions in both soil basal respiration and net N mineralization, indicating that liming has altered C and N cycling within this ecosystem. I also investigated how soil exchangeable Ca concentrations influence dissolved organic C and N retention. Soils higher in exchangeable Ca tended to release less C and N, suggesting that liming may facilitate Ca-organic matter bridging, thereby reducing C and N losses from the upper mineral soils.

BIOGRAPHICAL SKETCH

April Marin Melvin was born in a log cabin in rural Vermont. As a child, she spent her time exploring and horseback riding in the forests around her home. Through these experiences, she developed a great love of the outdoors and a desire to understand the natural world around her. April entered the University of Rochester in 1999 with every intention of pursuing a medial degree. Her interests quickly shifted though, and working with Dr. John Jaenike, conducted an independent research project studying the composition of the insect community within the leaf pitchers of *Sarracenia purpurea*, a carnivorous plant.

In 2003, having received her Bachelor of Science in Ecology and Evolutionary Biology, April left Rochester wanting to learn more about plants. She spent the summer of 2003 in North Carolina and southern Canada working with Jeremy Lichstein, a graduate student at Princeton University, mapping forest trees and quantifying sapling light availability. This experience peaked her interest in forest research and fueled her growing desire to investigate questions relating to human impacts on the environment. In fall 2003, April took a position as a research technician with Dr. Ram Oren at Duke University. While at Duke, she worked at the Free Air Carbon Dioxide Enrichment (FACE) Facility, a site where elevated concentrations of atmospheric carbon dioxide were pumped into a forest canopy to simulate future ambient carbon dioxide concentrations. Despite the heat, ticks, chiggers, copperhead snakes and poison ivy, April was excited by the research questions and collaborative work environment.

After a year at Duke, April followed her heart to Ithaca and worked briefly with Dr. David Stern at the Boyce Thompson Institute for Plant research, assisting in the molecular mapping of an algal genome. She entered Cornell in the fall of 2005 with intentions of pursuing carbon cycling research in northeastern forests. April soon realized that studying carbon is more

interesting (i.e. complicated) when you study it with important nutrients like nitrogen and calcium. She took on the challenge of working with soils and soon realized that if you have the patience to collect and process them, soils have much to tell us.

Throughout her graduate career, April has strived to understand how pollutants influence ecosystem health and nutrient dynamics. She has recognized that one way to reduce human impacts on the environment is through the implementation of sound science policy. Upon leaving Cornell, she travels first to Washington D.C., where she has a Mirzayan Science Technology Policy Fellowship at The National Academies. Working with the Board on Atmospheric Sciences and Climate, April will assist in the development of a report that will provide recommendations for advancing climate modeling in the United States. At the conclusion of this fellowship, April has a post-doctoral research position at the University of Florida, where she will work with Dr. Michelle Mack, studying the effects of fire on carbon and nitrogen cycling in the boreal forests of Alaska.

For my parents, Fern and Dennis

For supporting every decision I have ever made.

ACKNOWLEDGMENTS

This dissertation would not have been possible without the support of my many mentors, collaborators, peers, friends, and family.

First, I thank my advisor Christy Goodale, for being patient, encouraging, and allowing me to flounder a bit until I identified a project I found exciting. Christy has taught me to think critically and I deeply appreciate her support and feedback throughout this process. I also thank my committee members, Gary Lovett and Tim Fahey, for providing insights and assistance in the development of this work.

I have always had an interest in science, but my high school science teacher, Marjorie Salmon, made learning fun. I thank her for providing a solid foundation from which to build on. I became interested in ecological research working with John Jaenike and Kelly Dyer at the University of Rochester. They made lab work enjoyable and it was through their encouragement and guidance that I first considered pursing an advanced degree.

The members of the Goodale lab, including Marissa Weiss, Quinn Thomas, and Christina Tonitto, stimulated many interesting conversations and provided constructive feedback. A very special thanks to Guin Fredriksen, for keeping the lab running and providing me with assistants whenever I needed them. Brian Strahm helped me to bridge the gap between ecosystem ecology and soil science and greatly improved my understanding of soil processes. Sean Berthrong has been my science encyclopedia and an invaluable resource and friend since my days at Duke. Jenny Dauer, a fellow calcium-lover at Oregon State University, has been my go-to gal for calcium questions and has become a close friend and collaborator. My “mobile officemate,” Marc Goebel, was a great motivator during the last months of writing.

I collected and processed thousands of pounds of soil and it would not have been possible without the help of an army of field and lab assistants; Rebecca Sanders-DeMott, Jeff Beem-Miller, Rachel Hatch, Oliver Schaufelberger, Max Kraft, Amy Soriano, Jason Huck, Sarah Schneider, Erin Himes, Tim Huth, Wei Li, AJ Golash, Alicia Koral, Rebecca Daley, Joanna Blaszczak, Meredith Kueny, Maddie Stone, David Afable, Robert Levine, Moustafa Abou Areda, Laura Bertoia, and Tina Shah. I thank them all for being willing to get very fly-bitten, wet, and often very, very dirty.

Calcium is a challenging element to analyze at Cornell and I thank the many scientists at outside laboratories that ran samples for me, including Denise Schmidt at the Cary Institute of Ecosystem Studies, Chris Johnson and Mary Margaret Koppers at Syracuse University, and Jeff Merriam at the U.S. Forest Service. Additional laboratory analyses and assistance were provided by Kim Sparks, Joe Yavitt and Alexis Heinz.

The Woods Lake Watershed was a unique and challenging place to work and I thank the Woods Lake Co. for providing me site access and the use of their cabin. I especially thank my site contact Beth Pashley, for being so accommodating of my many, many trips to the watershed. Peter Smallidge provided me with plot information and raw data from this site and I am very grateful for his generosity. I also thank the investigators who had the foresight to initiate this long-term research project in 1989, when I was only 8 years old.

I am a better person and scientist because of the many EEB and BEB friends that I have made in the course of this journey. I cannot begin to convey my gratitude to you all. I thank Sara DeLeon and Michelle Schaut for making me smile and always listening. I also thank Dave Baker, who made our office a humorous environment and reminded me often that retaining sanity is important.

My greatest cheerleaders throughout this journey have been my family. I especially thank my parents, for their unwavering support for all the major decisions I have made in my life. I also thank Jason, for being my rock and having a degree of patience that I can only aspire to. He is the most resourceful person that I know and provided me with everything from exceptional meals to retrofitted field equipment. I am not sure I have would have made it without him.

My research was financially supported by the New York State Energy Research and Development Authority Environmental Monitoring, Evaluation, and Protection Program, the Cornell University Kieckhefer Adirondack Fellowship, the Biogeochemistry and Environmental Biocomplexity Small Grants Program, the Andrew W. Melon Foundation, the Agricultural Ecosystems Program, and Cornell University Graduate School.

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CHAPTER 1

Tree species effects on carbon, nitrogen, and calcium distribution in a Northeastern U.S. common garden

ABSTRACT

We investigated how tree species influence the distribution of carbon (C), nitrogen (N), and calcium (Ca) in forest soils in a 67-year old replicated common garden experiment. We focused on Norway spruce (*Picea abies*), red oak (*Quercus rubra*), and sugar maple (*Acer saccharum*) and expected that these three species would produce foliar litter with contrasting chemical composition, which would influence rates of organic matter turnover and nutrient accumulation within the forest floor and mineral soils. We hypothesized that Norway spruce would produce the most recalcitrant foliar litter, resulting in larger stocks of C and N within the forest floor of this species. We anticipated that sugar maple would produce the most labile litter and would also contain the greatest content of exchangeable Ca in the mineral soil, as has been observed in several studies in naturally occurring forests. We expected red oak to produce foliar litter of intermediate recalcitrance and exhibit intermediate forest floor C and N stocks. Mean annual leaf litter production did not differ significantly among species, however red oak foliar litter had the highest lignin concentration and a higher foliar C concentration than sugar maple. Norway spruce exhibited the largest forest floor mass, C, and N stocks and red oak had the smallest. The mean residence time for C and N in the forest floor was longest in Norway spruce plots and shortest in red oak. Across plots, residence time was strongly negatively correlated with earthworm density, but did not correlate with any measurement of litter chemistry. No differences in soil exchangeable Ca availability were observed. Most differences among species

were confined to the forest floor and top 7 cm of mineral soil. Our results suggest that foliar litter chemistry is not the primary control on soil nutrient cycling at this site and other factors, such as the presence of earthworms, can strongly influence organic matter turnover in ways that are unexpected when only considering litter chemistry.

INTRODUCTION

Individual tree species are often associated with differences in the biogeochemical cycling of essential elements, including carbon (C), nitrogen (N), and the dominant base cations calcium (Ca) and magnesium (Mg). In naturally established forests, variation in C, N, and base cation stocks within the forest floor and upper mineral soils under different tree species have been frequently documented (Finzi et al. 1998a, Finzi et al. 1998b, Dijkstra 2003, Fujinuma et al. 2005, Marcos et al. 2010). Differences in N and Ca mineralization rates have also been observed (Stump and Binkley 1993, Ste-Marie and Pare 1999, Dijkstra 2003, Lovett et al. 2004) and contribute to the general expectation that tree species can have large effects on ecosystem nutrient availability. Although these findings suggest tree species-level controls on nutrient cycling, many of these studies have been conducted in naturally established forests, where it is difficult to isolate the effects of plant species relative to inherent site characteristics. In addition to vegetation type, soil development is shaped by many other biotic and abiotic factors, including other biota, climate, soil parent material, topography, and time (Jenny 1941). These factors can impact both soil nutrient cycling and plant species establishment and distribution, thereby potentially underlying observed correlations between nutrient availability and individual tree species.

Common garden experiments provide an opportunity to isolate the effects of individual tree species on soil nutrient availability. In these experiments, individual species are planted in adjacent plots underlain by similar soils, to minimize differences in soil-forming factors and their possible role in determining plant species composition. Similar to studies in naturally established forests, some common garden studies have shown interspecific differences in C, N, and base cation pools in forest soils (Alban 1982, Binkley and Valentine 1991, Son and Gower 1992, Hagen-Thorn et al. 2004, Reich et al. 2005, Oostra et al. 2006, Vesterdal et al. 2008). These interspecific differences can be small however, and confined to the leaf litter and forest floor (Alriksson and Eriksson 1998) or the top few centimeters of mineral soil (Challinor 1968), indicating that species effects can be small when trees are planted on like soils and that differences are apparent primarily at shallow soil depths.

Plants facilitate important nutrient feedbacks that often differ among species and can contribute to observed variation in nutrient stocks and fluxes (Hobbie 1992). In the forest floor and surface mineral soils, chemistry of foliar litter inputs can have a strong influence on soil nutrient dynamics. Interspecific differences are commonly observed in the content of recalcitrant compounds in plant litter, such as lignin (Melillo et al. 1982, Ayres et al. 2009) and in C, N, and base cations (Alriksson and Eriksson 1998, Fujinuma et al. 2005, Reich et al. 2005, Vesterdal et al. 2008, Trum et al. 2011). Litter chemistry can affect microbial processing, where litter with high lignin concentrations or large lignin:N ratios exhibit slower rates of decomposition and N mineralization (Melillo et al. 1982, Gower and Son 1992, Stump and Binkley 1993, Sariyildiz et al. 2005, Hobbie et al. 2006). Calcium content can also affect litter breakdown by increasing soil pH and earthworm abundance (Reich et al. 2005, Hobbie et al. 2006), thereby stimulating both microbial (Haimi and Huhta 1990) and faunal-mediated decomposition (Hobbie et al. 2006).

As organic matter (OM) is decomposed, species' differences in nutrient cycling and leaching losses may influence nutrient movement and distribution within the soil profile. Interspecific differences have been document in the production and leaching of dissolved organic carbon and base cations (Dijkstra et al. 2001, Hagedorn and Machwitz 2007, Trum et al. 2011). Several studies have also shown that species vary in their ability to "pump" Ca, from deeper soil pools. Trees can redistribute Ca by taking up this nutrient from deep mineral soils, assimilating it into tissues, and later returning it to the soil surface as litter. Alban (1982) found that quaking aspen *(Populus tremuloides)* and white spruce (*Picea glauca*) contain nearly twice as much Ca in vegetation and forest floor pools relative to pine species (*Pinus reinosa, Pinus banksiana*) in adjacent stands, while the pines contained more Ca in mineral soils. He suggested that this was due to interspecific variation in Ca uptake and subsequent re-deposition of foliar litter of varying Ca content on the forest floor. Sugar maple (*Acer saccharum*) has also been linked to higher soil exchangeable Ca availability and increased Ca leaching losses compared to other species residing on soils of similar total mineral soil Ca content (Finzi et al. 1998a, Dijkstra and Smits 2002). These findings indicate that sugar maple may require more Ca and facilitate greater Ca cycling than co-occurring species in some forests. Soils beneath sugar maple have also been shown to exhibit significantly higher N mineralization rates than the conifer species eastern hemlock (*Tsuga canadensis*) and higher nitrification than both eastern hemlock and red oak (*Quercus rubra*) (Finzi et al. 1998b, Lovett et al. 2004). At the catchment-scale, nitrate leaching has been positively associated with the relative abundance of sugar maple and negatively associated with the abundance of red oak (Lovett et al. 2002).

We utilized a 67-year old common garden located in Ithaca, NY to investigate how sugar maple, red oak, and Norway spruce (*Picea abies*) affect the distribution of C, N, Ca and Mg

within the soil profile. Sugar maple and red oak often exhibit strong differences in foliar litter chemistry and N cycling, and therefore we hypothesized that they would have contrasting effects on soil nutrient pools, with larger accumulation of C and N expected under oak than maple. Norway spruce often exhibits lower foliar litter quality than deciduous species (Alriksson and Eriksson 1998, Augusto et al. 2002), and we expected to find a similar pattern at our study site. We hypothesized that Norway spruce would produce the most recalcitrant litter and exhibit the slowest rates of decomposition and forest floor turnover among the studied species, resulting in the greatest forest floor accumulation and soil C and N content. We expected that sugar maple foliar litter would have the most Ca, the lowest lignin concentration, and would decompose most quickly, leading to small C and N stocks in the forest floor and short C and N mean residence times. We also hypothesized that surface mineral soil exchangeable Ca content would be greatest beneath this species. To gain insights in C and N cycling that may not be apparent in the measurement of total C and N pools, we measured natural abundance $\delta^{13}C$ and $\delta^{15}N$ values in foliar litter and soils. We hypothesized that under sugar maple, rapid rates of C and N mineralization (Melillo et al. 1982, Lovett et al. 2004, Templer et al. 2007) would preferentially consume ^{12}C and ^{14}N through these loss pathways, resulting in the most enriched $\delta^{13}C$ and $\delta^{15}N$ values within the soil profile beneath this species. We expected Norway spruce would exhibit the least enriched isotopic values and that red oak would be intermediate. For all measured soil properties, we expected that species differences would be most evident in the forest floor and upper mineral soils and would decline with depth.

METHODS

Site description

Research was conducted at the Turkey Hill Plantations in Tompkins County, New York (42°27'0" N, 76°25'0" W, elevation 430 m). Mean annual precipitation for the site is 939 mm per year and the mean annual temperature is 7.8° C (Northeast Regional Climate Change Center, 2010) . Between 1938 and 1940, Dr. Robert F. Chandler established 0.4 ha single-species plots to study how 13 different tree species influence soil properties. For our study, we focused on replicated, monospecific plots of sugar maple, red oak, and Norway spruce (> 70 % of plot biomass is the focal species; Table 1.1). We expected these three species to exhibit differences in the quality of foliar litter inputs and rates of C, N, and base cation cycling.

Soils at the Turkey Hill Plantations are developed from silt-enriched glacial till derived from local sandstone and siltstone. Soils are coarse-loamy mixed mesic Typic Fragiudepts (Bath, Mardin Series) and Typic Dystrudepts (Lordstown Series) and are moderately well-drained and acidic (Riha et al. 1986). The site was cultivated for approximately 100 years prior to tree planting, resulting in a vertically homogenized plow horizon to a depth of 20 cm (Young 1981). Trees were planted in 1.5 m x 1.5 m spacing and received little management after planting. Non-native earthworms are present in all plots, with densities varying by tree species and plot. The earthworm community is dominated by *Lumbricus* species, with *L. terrestris* exhibiting the highest densities in most plots. Other species included *L. rubellus*, *L. castaneus*, *Dendrobaena octaedra*, *Octolasion tyrataeum*, and *Eisenia* and *Aporrectodea* species (Suarez 2004). Unfortunately, pre-planting soil nutrient data was unavailable, so our analyses focus on identifying relative differences among current nutrient pools.

Table 1.1. Focal and non-focal tree species biomass and basal area in studied plots at the Turkey Hill Plantations, Ithaca NY.

		Aboveground live biomass kg m^{-2}		Basal area m^{-2} ha^{-1}	
Species	Plot	Focal Species	Non-focal species	Focal Species	Non-focal species
Norway Spruce	1	23.4	1.1	47.4	1.8
Norway Spruce	2	19.8	7.3	41.1	10.7
Red Oak	1	31.3	0.8	41.6	1.4
Red Oak	2	38.2	0.02	48.6	0.05
Sugar Maple	1	23.5	0.6	33.3	0.9
Sugar Maple	2	18.8	6.7	26.0	9.3

Soil and forest floor samples were collected between June 21 and July 1, 2006. Samples were collected at least 5 m inside the plot perimeter, to reduce edge effects. Within each plot, six 15 cm x 30 cm forest floor blocks were collected from locations distributed throughout each plot. After removing the whole forest floor, six 2.5 cm diameter soil cores were collected from underlying mineral soil, each sampled incrementally for depths 0 - 7 cm, 7 - 14 cm, 14 - 20 cm and 20 - 40 cm. In locations where 40 cm could not be reached because of rocks or coarse roots, cores were taken from as deep as possible and actual depth was recorded. The six samples collected within each block were combined for each depth, yielding 6 composite soil samples per depth, per plot.

Aboveground litter was collected for one year, beginning in early September 2006. Twelve 0.23 m^2 litter baskets (40.6 cm x 55.9 cm) were distributed across each plot. Baskets were secured in place with stakes and lined with fiberglass mesh window screen to prevent litter material from resting on the bottom of the basket. Collections were made monthly throughout the growing season and bi-weekly during peak litter fall (October to November). Litter was sorted into components including: focal species foliage, non-focal species foliage, seeds of the focal species, seeds of non-focal species, branches, pollen cones, seed cones, and miscellaneous components (e.g. insects). In the fall of 2006, the diameter at breast height (dbh) was measured on all trees within each plot. Plot biomass was calculated using allometric equations obtained from Jenkins et al. (2003).

Laboratory Analysis

Mineral soils and forest floor samples were air dried for at least two weeks, then passed through 2 mm and 5.6 mm sieves, respectively. Subsamples of mineral soil and forest floor were ground to a fine powder for C and N analysis using a Retsch Mixer Mill, type MM200. Foliar material was ground using a cyclone sample mill. Total C and N were measured with a Vario EL III elemental analyzer. Mineral soil, forest floor, and focal species foliage samples were also analyzed for $\delta^{13}C$ and $\delta^{15}N$ at the Cornell Stable Isotope Laboratory, Ithaca NY, using a Thermo Delta V isotope ratio mass spectrometer. Soil pH analysis was performed using an Accumet basic AB15 pH meter with a flushable junction soil probe. A 10 g subsample of soil was mixed thoroughly with 20 mL of deionized water. After a 30-minute equilibration, samples were gently swirled and a reading was taken after pH stabilized.

Mineral soil exchangeable cations were extracted using 1 *M* ammonium chloride (NH_4Cl). Five grams of mineral soil were mixed with 50 mL of NH_4Cl and placed on a shaker table for 1 hour. Following shaking, solutions were vacuum filtered through Gelman A/E glass fiber filters. Extracts were kept frozen until analysis. Total elemental digestion of mineral soil and focal species foliar litter was performed by the Cornell Nutrient Analysis Laboratory using EPA Method 3051. Briefly, 0.5 g of sample was mixed with 5 mL of nitric acid (HNO_3) and microwaved for 20 minutes. Afterward, samples were diluted to a 50 mL, 10 % HNO_3 solution. Exchangeable and total Ca and Mg were analyzed using inductively coupled plasma emission spectroscopy at the Cary Institute of Ecosystem Studies, Millbrook NY. Foliar litter lignin content was determined on a composite sample of foliar litter of the focal species for each plot by the Dairy One Forage Laboratory, Ithaca NY. Samples were digested using the ANKOM A200 filter bag technique. Each sample was placed in a filter bag and submerged for 75 minutes

in acid detergent fiber solution in an ANKOM A200 Digestion Unit. Next, the samples were rinsed with boiling water, followed by acetone, then dried at 100^{o} C for two hours. The remaining residue was then combined with 72 % sulfuric acid for 3 hours in an ANKOM A200 DaisyII Incubator. Sample lignin concentration was then determined using a FOSS NIRSystems Model 6500 VIS-NIR Spectrometer.

Mean residence time (MRT) for C and N in the forest floor was determined as discussed in Gosz et al. (1976). That is, MRT (years) was estimated as the total C or N in the forest floor (g m^{-2}) divided by total annual aboveground litter C or N input (g m^{-2} yr^{-1}). This approach provides an upper limit on C and N MRTs, as it does not include C or N inputs from throughfall or belowground sources. It also assumes that the forest floor is in a steady state with respect to the current litter inputs. For our analysis, we excluded acorns and Norway spruce seed cones that were present in litter baskets and the forest floor because they were heterogeneously distributed within plots and rarely found in litter baskets. After removing these components, 99 % of annual litterfall was comprised of foliar litter and branches. Focal species foliar litter accounted for > 80 % of foliar inputs in four of the studied plots and total foliar litter C and N inputs were estimated using focal species C and N data. Two plots contained high non-focal species ingrowth by species that were the focal species in other plots. In these cases C and N estimates were made using data collected from the appropriate focal species plot. Carbon and N inputs from branch litter were estimated using wood percent C and N values for the focal species obtained from other forested sites in the Ithaca area (Goodale, unpublished). Red oak and sugar maple data were available and Norway spruce values were estimated using data from eastern hemlock.

Worm densities were estimated by Suarez (2004) in 2001 using a liquid extraction method (Raw 1959). Six 50 cm x 50 cm squares within each plot were wet with 8 L of 0.4 %

formalin after removing the surface litter. All worms in the litter and those that emerged from the soil within 10 minutes of wetting were counted, weighed, and identified by species.

Statistical analysis was performed using JMP 7.0 (SAS Institute). A mixed model was used, with species as a fixed effect and a species by plot interaction as a random effect. After confirming main effects, mean comparisons were made using Tukey's test ($P < 0.05$). Analysis of the relationship between earthworm density and forest floor C and N MRTs was determined using log transformed data.

RESULTS

Mean annual aboveground litter production averaged 449 g OM m^{-2} yr^{-1} and did not differ significantly among species (Table 1.2). The Norway spruce plots produced the least amount of foliar litter material (including both focal and non-focal species), and the greatest amount of non-foliar litter, which was comprised largely of seed cones. Red oak foliar litter exhibited a significantly higher C concentration than sugar maple while the C concentration of Norway spruce foliage did not differ from either species (Table 1.3). Sugar maple had a significantly lower N concentration than both Norway spruce and red oak. The C:N ratio of sugar maple foliar litter was significantly larger than Norway spruce, and red oak did not differ from either species. Norway spruce exhibited significantly more enriched $\delta^{13}C$ values in foliar litter than the hardwood species, while litter $\delta^{15}N$ did not differ among the three species (Table 1.3). Red oak foliar litter had the highest lignin concentration and lignin:N ratio, while sugar maple values were the lowest. Red oak foliar litter Ca content was the lowest among studied species, but this difference was not statistically significant. Magnesium content was significantly lower in the Norway spruce foliar litter relative to the hardwood species.

Table 1.2. Aboveground litter mass (g organic matter m^{-2} yr^{-1}) for each studied species. Mean values are given ± SE (n = 2 plots).

Litter component	Norway Spruce	Red Oak	Sugar Maple
Foliage - non-focal species	73 ± 34	51 ± 19	43 ± 30
Bark and branches	102 ± 21	93 ± 57	71 ± 35
Seeds - focal species	1 ± 1	14 ± 12	32 ± 11
Seeds - non-focal species	1 ± 0.4	6 ± 6	4 ± 5
Cones - pollen	1 ± 0.4 [a]	0 ± 0 [b]	0 ± 0 [b]
Cones - seed	55 ± 62 [a]	0 ± 0 [b]	0 ± 0 [b]
Miscellaneous	1 ± 1	1 ± 2	0.4 ± 1
Total	455 ± 73	440 ± 83	451 ± 50

Table 1.3. Foliar chemistry for plot focal species. Row values with different letters indicate a significant difference among species ($P < 0.05$). Mean values are reported ± SE (n = 2 plots). Percent lignin and lignin:N ratio values are the mean of one sample per species plot.

Foliar Chemistry	Norway Spruce	Red Oak	Sugar Maple
C (mg g^{-1})	519.4 ± 3.0 ^{ab}	533.7 ± 3.4 ^{a}	509.1 ± 5.6 ^{b}
N (mg g^{-1})	11.2 ± 0.8 ^{a}	11.1 ± 0.9 ^{a}	10.2 ± 0.6 ^{b}
C:N ratio	46.7 ± 3.1 ^{a}	48.7 ± 3.9 ^{ab}	50.4 ± 2.9 ^{b}
$\delta^{13}C$ (‰)	-27.4 ± 0.2 ^{a}	-28.7 ± 0.2 ^{b}	-29.2 ± 0.3 ^{b}
$\delta^{15}N$ (‰)	-0.1 ± 0.2	-0.1 ± 0.3	-1.1 ± 0.3
Lignin (%)	23.0	31.8	17.3
Lignin:N ratio	20.5	28.6	17.0
Ca (mg g^{-1})	11.7 ± 1.0	8.8 ± 0.6	12.8 ± 1.7
Mg (mg g^{-1})	0.6 ± 0.1 ^{a}	1.4 ± 0.1 ^{b}	1.6 ± 0.2 ^{b}

The forest floor mass in Norway spruce plots was significantly larger than in red oak and sugar maple plots, resulting in greater C and N stocks in the forest floor of this species (Table 1.4). Forest floor MRTs did not correlate significantly with foliar litter C:N ratio ($R^2 = 0.35$, $P = 0.22$), lignin content ($R^2 = 0.06$, $P = 0.65$), lignin:N ratio ($R^2 = 0.10$, $P = 0.54$), or Ca content ($R^2 = 0.001$, $P = 0.95$), but were strongly negatively correlated with plot earthworm densities (Figure 1.1; $R^2 = 0.85$, $P < 0.01$ for C MRT and $R^2 = 0.95$, $P < 0.001$ for N MRT). Red oak plots contained the highest earthworm densities and shortest forest floor MRTs while Norway spruce had the lowest densities and longest residence times. The sugar maple plots exhibited intermediate earthworm densities, but also showed greater variability in C and N MRTs, presumably as a result of a large difference in earthworm densities between the two plots of this species.

To test our hypothesis that faster decomposition would result in greater $\delta^{15}N$ and $\delta^{13}C$ values, we calculated a relative isotopic enrichment for each plot as the difference between foliar litter and forest floor $\delta^{15}N$ and $\delta^{13}C$ values and compared these values to forest floor MRT. Relative $\delta^{15}N$ enrichment was close to zero for all plots except one of the sugar maple stands, which showed a $\delta^{15}N$ enrichment of 4.5 ‰ (Figure 1.2). One of the Norway spruce stands and both the red oak plots exhibited negative $\delta^{15}N$ enrichment values, in that $\delta^{15}N$ values were lower in the forest floor than in foliar litter. A similar pattern was observed for $\delta^{13}C$ enrichment (data not shown). These results suggest that there is little fractionation occurring during the initial breakdown of foliar litter.

In the mineral soil, concentrations of C and N in the 0 - 7 cm depth increment were significantly greater for Norway spruce than for sugar maple and red oak (Figure 1.3A and B). The C:N ratio of Norway spruce soil was significantly larger than red oak to a depth of 14 cm

Table 1.4. Forest floor C and N stocks and fluxes.

Forest floor	Norway Spruce	Red Oak	Sugar Maple
C:N ratio	28.9 ± 0.9	30.2 ± 2.4	26.3 ± 3.0
Total C stocks (g m^{-2})	1263	463	519
Total N stocks (g m^{-2})	32	9	13
Annual C input (g m^{-2} yr^{-1})	203	219	210
Annual N input (g m^{-2} yr^{-1})	3	4	4
Residence time (yrs)	5	1	2
C residence time (yrs)	6	2	3
N residence time (yrs)	10	2	4

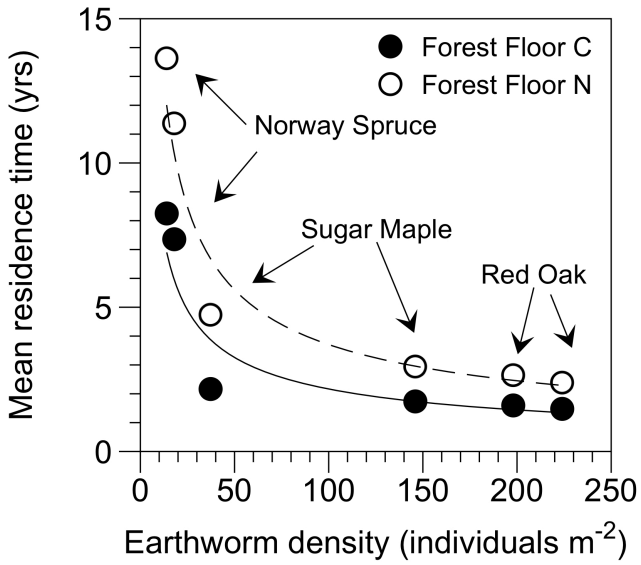

Figure 1.1. Forest floor C and N mean residence time as it relates to plot earthworm density. Earthworm density data obtained from Suarez (2004).

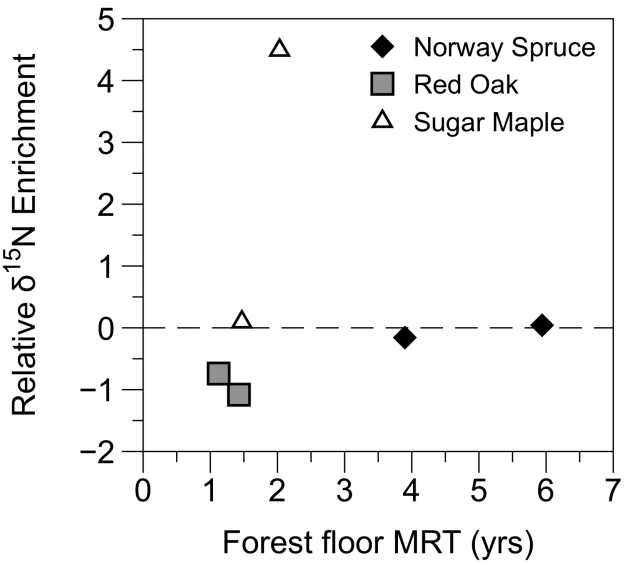

Figure 1.2. Estimated forest floor mean residence time and relative $\delta^{15}N$ enrichment (forest floor $\delta^{15}N$ – foliar $\delta^{15}N$) for each studied species plot.

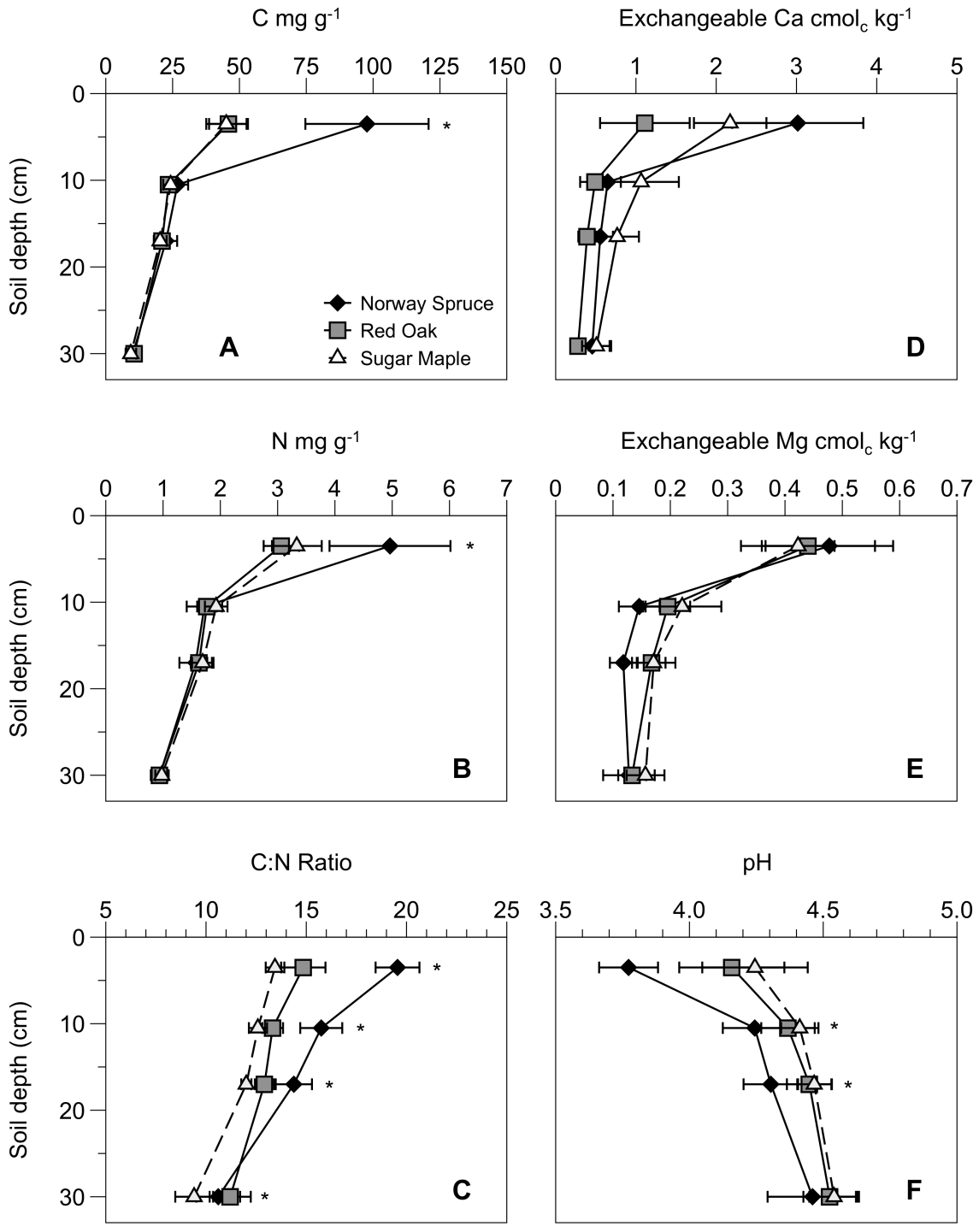

Figure 1.3. Soil properties by depth increment for each tree species. Significant differences among species for a given depth are represented by * ($P < 0.05$). Error bars indicate ± SE (n = 2 plots).

and greater than sugar maple to 20 cm depth (Figure 1.3C). The difference in C:N was driven by slightly higher C concentrations in Norway spruce soils. In the mineral soils collected at depth 20 - 40 cm, the C:N ratio of red oak soils was higher than for sugar maple while Norway spruce did not differ significantly from either hardwood species.

Norway spruce exhibited significantly more enriched $\delta^{13}C$ values in the 0 - 7 cm mineral soil depth increment than the other two species (Figure 1.4A). For the 7 - 14 cm depth increment, Norway spruce $\delta^{13}C$ values were significantly higher than sugar maple while red oak did not differ from either. Significant differences among species in $\delta^{13}C$ values were not present in the forest floor or other mineral soil depths. The only significant difference in $\delta^{15}N$ values among species occurred in the 20 - 40 cm depth increment, where red oak soils were more enriched than sugar maple and Norway spruce did not differ from either species (Figure 1.4B). The relative enrichment in $\delta^{13}C$ and $\delta^{15}N$ values between the forest floor and the 20 - 40 cm mineral soil depth increment differed among species (Figure 1.4A and B). Soils under red oak showed the greatest relative enrichment in $\delta^{13}C$ and $\delta^{15}N$ values, with a mean increase of 3.9 ‰ in $\delta^{13}C$ and 6.2 ‰ $\delta^{15}N$. Soils under sugar maple showed little change in isotopic values with depth, with an increase of 1.4 ‰ in $\delta^{13}C$ and 2.6 ‰ in $\delta^{15}N$.

Exchangeable Ca and Mg did not differ significantly among species for any measured depth (Figure 1.3D and E). Similarly, total soil Ca did not differ among species at any depth (data not shown). Values for exchangeable Ca and Mg were highest and most variable in the 0 - 7 cm mineral soil increment and declined with depth. Soil pH increased with depth for all species (Figure 1.3F). Norway spruce exhibited a lower pH value than both red oak and sugar maple in the 0 - 7cm depth increment (3.7 vs. 4.2 for both hardwood species), but this difference was not statistically significant. In the 7-14 cm depth increment, Norway spruce pH was significantly

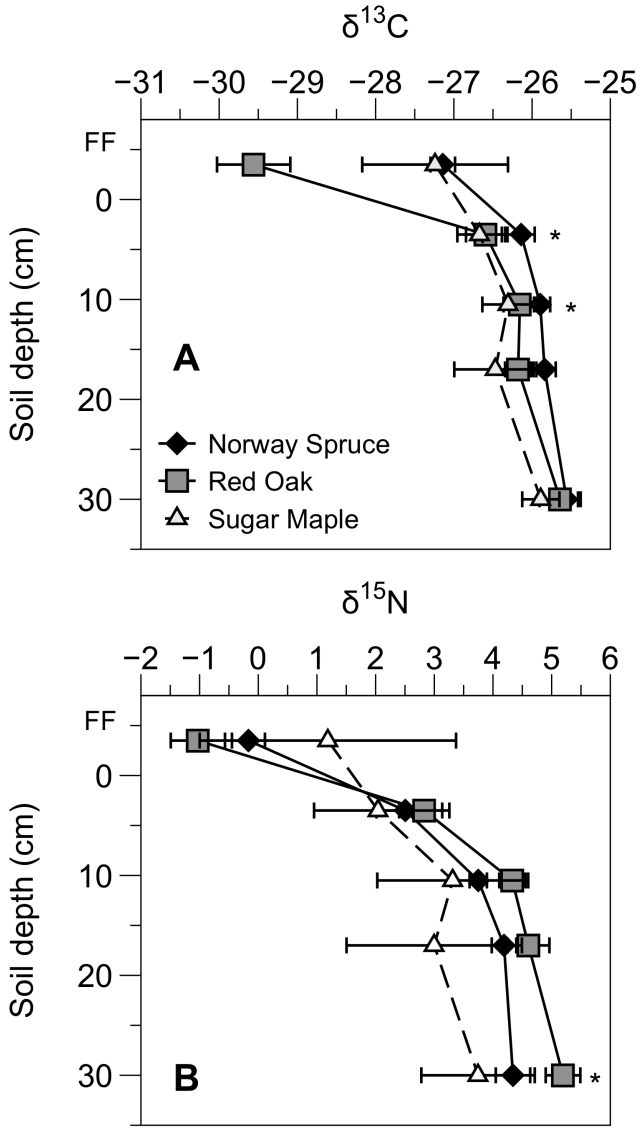

Figure 1.4. $\delta^{13}C$ and $\delta^{15}N$ values for forest floor (FF) and mineral soils collected in plots of each tree species. * represents a significant difference among species for the given depth ($P < 0.05$). Error bars indicate ± SE (n = 2 plots).

lower than sugar maple and at 14 - 20 cm depth, was significantly lower than both hardwood species.

DISCUSSION

We expected that Norway spruce, red oak, and sugar maple would have differential impacts on soil nutrient pools and hypothesized that these differences would be influenced by interspecific variation in the quantity of aboveground litter inputs and litter chemistry. We observed some differences in foliar chemical composition and nutrient distribution, but they were not always the relationships we had anticipated. As hypothesized, Norway spruce contained the largest C and N stocks in the forest floor. However, this species exhibited the lowest foliar litter C:N ratio and intermediate lignin concentration and lignin:N ratio, relative to the other species. Conifer species, including Norway spruce, often have higher lignin concentrations and foliar C:N and lignin:N ratios than deciduous species (Alriksson and Eriksson 1998, Augusto et al. 2002), and these foliar characteristics generally correlate with slower rates of decomposition and greater OM accumulation (Melillo et al. 1982, Sariyildiz et al. 2005). Others however, have shown that the relationship between N mineralization and litter lignin and lignin:N ratios can be weak and unable to explain interspecific differences in N cycling (Lovett et al. 2004). Our findings suggest that foliar litter chemistry is not the primary control on forest floor turnover at our study site and that OM accumulation may be influenced more strongly by factors controlling earthworm abundance.

Within the mineral soil, Norway spruce exhibited significantly greater C:N ratios to a depth 20 cm. Prior to the establishment of the common garden experiment at the Turkey Hill Plantations, the entire site was plowed, vertically homogenizing the upper 20 cm of mineral soil.

Assuming that the soils beneath all species plots are similar to one another, our results suggest that that the observed difference in soil C:N ratio is due to the influence of Norway spruce on the vertical distribution of soil C and N pools. The difference in C:N ratio is driven by slightly higher C concentrations in Norway spruce soil. Harris and Riha (1991) found that Norway spruce forest floor has a relatively lower decay rate constant than sugar maple at this site, while Phillips and Fahey (2006) found Norway spruce to have a significantly lower C mineralization rate than red oak, suggesting that the higher C concentration may be driven by reduced C mineralization in the soils beneath Norway spruce. However, it remains unclear what factors may be regulating this slower rate of decomposition, as it does not appear to be driven by litter chemistry.

Similarly, litter chemistry did not predict C or N turnover under red oak, the species with the greatest lignin:N ratio and the most rapid forest floor C and N turnover times. Instead of litter chemistry, turnover appears to be controlled largely by the high earthworm density beneath this species. Other studies have shown that higher foliar Ca concentration and soil exchangeable Ca availability are correlated with greater earthworm abundance (Reich et al. 2005). At the Turkey Hill Plantations, red oak exhibited the lowest foliar litter Ca concentrations and smallest mineral soil Ca pools, although these differences were not significant. Earlier work at this site found that small topographical differences across the landscape influence soil moisture and that soil moisture is strongly positively correlated with earthworm density (Suarez 2004). Tree species was also a significant predictor of earthworm abundance, independent of differences in soil moisture. These findings indicate that soil heterogeneity driven by small-scale differences in abiotic factors can exert strong controls on soil biota, which in turn can lead to large changes in soil chemistry and ecosystem nutrient cycling.

Soils beneath all tree species became relatively enriched in $\delta^{13}C$ and $\delta^{15}N$ with soil depth, a pattern that is commonly found in forest ecosystems (Nadelhoffer and Fry 1988, Tu and Dawson 2005, Hobbie and Ouimette 2009). Soils under the two ectomycorrhizal tree species, Norway spruce and red oak, showed a trend toward greater relative isotopic enrichment between the forest floor and 20 - 40 cm mineral soil depth compared to the arbuscular mycorrhizal species sugar maple. This difference in $\delta^{15}N$ with depth by mycorrhizal association was noted in a review by Hobbie and Ouimette (2009), who attributed this pattern in part to greater discrimination against ^{15}N by ectomycorrhizal species during N transfer to the host plant, resulting in lower $\delta^{15}N$ values in the forest floor and upper mineral soils and higher $\delta^{15}N$ at depth.

Minimal differences in the quantity of litter produced, as well as the C, N, Ca, and Mg concentrations of foliar litter indicate that aboveground OM and nutrient inputs are similar among species at this site. Differences in nutrient accumulation therefore, are likely driven by variation in OM turnover time and not inputs. The differences we did see were primarily in the surface soils, a finding commonly observed in tree species studies (Challinor 1968, Alriksson and Eriksson 1998), yet our results differ from others in that forest floor accumulation and nutrient MRTs across species are correlated primarily with earthworm density and not litter recalcitrance. Many of the differences we observed were small, but given the size of C and N stocks in soils, it can be difficult to detect small changes relative to background concentrations and inherent soil heterogeneity. Previous investigation of C and N cycling at our site shows that sugar maple forest floor material has relatively higher soil respiration and N mineralization rates than Norway spruce (Harris and Riha 1991), which is consistent with our estimates of forest floor C and N turnover for these two species. Similarly, Phillips and Fahey (2006) found

significantly higher C mineralization in the top 4 cm of mineral soils in red oak plots than in Norway spruce, while sugar maple did not differ from either species. They also found that rates of net N mineralization rates were significantly higher in sugar maple soils relative to red oak, a result that contrasts with our estimate of shorter N residence time in red oak forest floors relative to sugar maple.

Some common garden studies have found greater interspecific differences among similar species than we observed. Reich et al. (2005) found strong correlations between exchangeable Ca content and earthworm biomass to a depth of 40 cm beneath species including Norway spruce, red oak, and two maple species (*Acer pseudoplatanus* and *Acer platanoides*). Cation exchange capacity, base saturation, and soil pH were also higher in maple plots relative to Norway spruce and red oak. Son and Gower (1992) observed significantly larger forest floor mass and N stocks beneath Norway spruce relative to red oak. In the top 30 cm of mineral soil Norway spruce also had significantly lower pH and exchangeable Ca content. Other studies though, have shown small or limited differences among tree species (Challinor 1968, France et al. 1989).

The magnitude of interspecific differences could be influenced by inherent soil properties and nutrient content. When nutrient availability is high, interspecific differences in physiological nutrient requirements may allow for differential nutrient acquisition and greater divergence in the chemistry of OM inputs. This can contribute to positive feedback loops that differ among species, leading to greater interspecific differences under high soil nutrient conditions. Variation in soil properties such as base cation content can affect soil acidity, and directly impact OM decomposition. Berger et al. (2002) found significantly higher C and N stocks in the forest floor and 0 - 50 cm mineral soil of Norway spruce stands versus adjacent spruce-mixed hardwood

stands in relatively nutrient rich soils, while no difference was evident for the same species on a more acidic, nutrient poor site. They found interspecific differences to be predicted by the presence of spruce and base cations and anions, including Ca. Aluminum was correlated with C stocks at the less fertile site, indicating the importance of soil pH in influencing soil nutrient pools. Raulund-Rasmussen et al. (1995) found that forest floor N and exchangeable Ca and Mg stocks were significantly higher beneath Norway spruce compared to English oak (*Quercus robur*) planted on relatively fertile soils, but observed no differences in these nutrient pools at a sandy soil site. The presence of earthworms in the oak soils at the fertile site may have contributed to observed differences in forest floor nutrients, but forest floor C stocks differed between these two species in both fertile and nutrient poor soils.

We were surprised to find few effects of sugar maple on soil nutrient pools. Based on previous studies (eg. Finzi et al. 1998a, Dijkstra 2003, Fujinuma et al. 2005), we expected this species to exhibit greater exchangeable Ca availability caused by Ca "pumping". We also hypothesized that this species would exhibit higher rates of N cycling (as observed by Phillips and Fahey 2006), resulting in greater relative soil $\delta^{15}N$ enrichment, but we did not observe this pattern. Most of the studies showing sugar maple effects on Ca and N cycling have been conducted in naturally established forests. This highlights the importance of common garden experiments and the possibility that the commonly observed association of sugar maple with high Ca soils and high N cycling could be largely the result of preferential establishment in relatively fertile soils.

Plant-soil interactions play an important role in biogeochemical cycling, yet our understanding of how this relationship influences stand-level soil nutrient pools is limited. Our findings indicate that litter chemistry is not always the dominant driver of OM turnover and that

small differences in abiotic factors, such as soil moisture, can influence earthworm abundance, resulting in dramatic effects on ecosystem-scale nutrient dynamics. Refining our understanding of processes dictating nutrient cycling is especially important in forests where species composition is predicted to change in response to climate change (Iverson and Prasad 1998), pests and pathogens (Lovett et al. 2006), and increased N deposition (Thomas et al. 2010).

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CHAPTER 2

Effects of liming on DOC and DON sorption in acidic forest soils

ABSTRACT

In acid-impacted forests, changes in soil pH and exchangeable calcium content may influence the adsorption of DOC and DON, leading to consequences for ecosystem C and N balance. We investigated the long-term effect of a calcium carbonate (lime) addition on DOC and DON sorption in soils collected from the Woods Lake Watershed, Adirondack Park NY. Using initial mass isotherms, we found that liming decreased losses of DOC and DON from the upper 20 cm of mineral soil relative to unlimed soils. The top 20 cm of mineral soil were a source of DOC and DON within all treatments, reflecting large quantities of native DOM within this ecosystem. Retention of DOC and DON increased with soil depth and there was a tendency for greater retention with increasing initial concentrations of added DOM. These findings suggest that changes in soil properties associated with liming can reduce DOC and DON mobility within the upper mineral soils, which could have implications for forest C and N cycling.

INTRODUCTION

Sorption of dissolved organic matter (DOM) in soils is an important process in the retention of carbon (C) and nitrogen (N) in forest ecosystems (Kaiser and Guggenberger 2000, Kalbitz et al. 2005). When DOM adsorbs to soil surfaces, leaching losses are reduced, decomposition decreases, and mean residence times of dissolved organic carbon (DOC) and nitrogen (DON) increase (Qualls and Haines 1991, Kalbitz et al. 2005). In recent years, a trend

toward higher DOC concentrations in surface waters has been observed across the northeastern U.S. and parts of Europe (Driscoll et al. 2003, Stoddard et al. 2003, Evans et al. 2006, Monteith et al. 2007). This increase has been attributed in part to reduced sulfate (SO_4^{2-}) deposition, which can decrease soil water acidity and ionic strength, leading to increased solubility and export of DOC from soils (Evans et al. 2006, Monteith et al. 2007). The record of DON measurements is shorter, but there is an expectation that DON will follow a similar trend (Evans et al. 2005). These regional patterns suggest that acidification can have large-scale effects on C and N export in temperate ecosystems, yet the relationship between soil acidification and DOM retention remains poorly understood. Further, it is unclear how management practices designed to reduce acidification, such as liming, may affect DOC and DON retention.

The effects of acidification on sorptive processes are complex and often vary among studies and soil horizons. Acid deposition decreases soil pH (van Breemen et al. 1983, Driscoll et al. 2001), increases aluminum (Al) mobility (Cronan and Schofield 1990), and leads to losses of exchangeable base cations, including calcium (Ca) (Likens et al. 1996, Driscoll et al. 2001). As these soil properties change, they can impact DOM retention through a variety of mechanisms. Within the forest floor and mineral A horizon, increased DOM retention is often correlated with decreasing pH (Godde et al. 1996, Kalbitz et al. 2000). This is attributed to increased protonation of organic matter (OM) functional groups and subsequent changes in steric conformation that reduce DOM mobility (Tipping and Hurley 1988, Kalbitz et al. 2000). The effects of declining pH in the B and C horizons seem to be driven at least in part by soil type. For instance, iron oxides and aluminum hydroxides tend to exhibit enhanced DOM retention in the B and C horizons. This retention is attributed to increased positive surface charge and enhanced bridging between DOM and these positive surfaces, as well as increased ligand exchange (Davis 1982, Gu

et al. 1994, Kalbitz et al. 2000). In contrast, experiments with spodosols generally show either reduced retention of DOM with decreased pH (David et al. 1989, Jardine et al. 1989, Guggenberger et al. 1994) or no effect (Cronan 1985, Vance and David 1992). Reduced retention has been attributed to increased solubilization of metal-DOM complexes caused by proton competition (Kalbitz et al. 2000). Studies showing little change in DOM retention suggest that inherent soil properties, such as buffering capacity and inherent soil OM content may have a greater influence on DOM retention that may mask any pH effect (Moore et al. 1992, Vance and David 1992, Michalzik et al. 2001). This variability in response among horizons and soil types makes it difficult to quantify how acidification influences DOC and DON export to surface waters.

In addition to changes in soil pH, acidification alters soil exchangeable cation availability. Acidification enhances mobilization of aluminum (Al) (Cronan and Schofield 1990), which can facilitate enhanced Al-OM cation bridging and increase DOM retention (Oades 1988). Acidification also leads to a net loss of exchangeable base cations, including calcium (Ca) (Likens et al. 1996, Driscoll et al. 2001). Calcium is typically the most abundant base cation on the soil exchange complex and is important in neutralizing acids in soil (Likens et al. 1998, Driscoll et al. 2001). In neutral and alkaline soils, Ca has been shown to stabilize DOM and enhance retention by a similar mechanism to that of Al in acid soils (Sposito 1984, Oades 1988, Mikutta et al. 2007). Calcium-OM bridging has been explored little in forest soils due to the generally low soil pH and exchangeable Ca availability. However, this mechanism of DOM retention could become more important when Ca is applied as a management strategy, to ameliorate the effects of acidification.

Addition of lime ($CaCO_3$) to acid forest soils typically increases pH and exchangeable Ca availability and reduces Al mobility. These changes influence both physical and biological processes in soils which can alter DOC and DON dynamics and retention. The solubility of DOM tends to increase as pH rises because of the deprotonation of functional groups (Tipping and Hurley 1988). Microbial activity can also be stimulated, resulting in enhanced DOC and DON production and increased leaching losses in the O and A horizons (Anderson 1998, Andersson et al. 2000). The chemical composition of DOM can also shift with liming, resulting in higher concentrations of hydrophilic acids relative to hydrophobic (Andersson and Nilsson 2001). Hydrophobic compounds sorb more readily to soil surfaces, are often comprised of more recalcitrant OM, and tend to have lower N concentrations with larger DOC:DON ratio than hydrophilic compounds (Qualls and Haines 1992, Gu et al. 1995, Kaiser et al. 1996, Kaiser and Guggenberger 2000, Nilsson et al. 2001). These findings suggest that liming may enhance DOC and DON losses from soils as a result of increased DOM production and solubility, and reduced sorption of produced DOM. Other work however, indicates that addition of Ca can suppress microbial activity (Groffman et al. 2006), that changes in DOM chemistry may be small, and that DOM sorption can increase with liming, despite higher production rates of DOC and DON (Nilsson et al. 2001). Further, increased Ca availability has been shown to increase DOC precipitation, flocculation, and retention (Tipping and Ohnstad 1984, Romkens and Dolfing 1998, Oste et al. 2002), indicating that liming could enhance DOM retention in some ecosystems, thereby reducing DOC and DON export.

We studied the long-term effects of soil liming on the sorption of DOC and DON in forest soils, isolating the potential roles of changes to soil properties and DOM composition in response to liming. In 1989, lime was added to two subcatchments within the Woods Lake

Watershed in the Adirondack Park, NY, to ameliorate the acidification of surface waters. Soil solution pH and Ca concentrations increased in the limed subcatchments shortly after the lime addition and they remained elevated for the three years of study following treatment (Geary and Driscoll 1996). Soil water DOC concentrations increased in one of the limed subcatchments immediately following liming, but returned to pre-treatment levels within a few months. The second limed subcatchment showed no increase in soil solution DOC concentrations (Geary and Driscoll 1996). Elevated DOC concentrations were also observed in streams draining both limed subcatchments immediately following the addition, but declined within a few months of addition (Cirmo and Driscoll 1996). These findings indicate that the ecosystem-scale changes in DOM retention in the Woods Lake Watershed were transient. However, no prior studies at this site have investigated the effects of increased pH and exchangeable Ca availability on sorptive processes. We hypothesized that the liming would increase both soil pH and exchangeable Ca availability and that these changes would facilitate greater DOC and DON sorption in treated soils relative to controls. We conducted a series of batch equilibration sorption experiments using DOM extracts and mineral soils from multiple depths collected within limed and unlimed subcatchments to investigate these processes.

METHODS

Site description

Mineral soil and DOM were collected from the Woods Lake Watershed, located in the Adirondack Park, NY (43^{o} 52’ N, 74^{o} 57’ W). This watershed has 98% forest cover (Staubitz and Zarriello 1989) and is dominated by American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), and yellow birch (*Betula alleghaniensis*), with lesser quantities of red spruce (*Picea*

rubens), sugar maple (*Acer saccharum*), and striped maple (*Acer pensylvanicum*) (Smallidge and Leopold 1994). The site is underlain by hornblende granitic gneiss bedrock covered by a sandy glacial till comprised of quartz and feldspar, with some interspersed hornblende, ilmenite and magnetite (April and Newton 1985). The soils are classified as Orthod spodosols (Smallidge and Leopold 1994) and mineral soils average 30 to 35 cm deep (Brocksen et al. 1988). In 1989, lime was applied to two ~50 ha subcatchments in a single application of 6.89 tons ha^{-1} (2.76 t Ca ha^{-1}) in a project known as the Experimental Watershed Liming Study (Driscoll et al. 1996). Two additional subcatchments were maintained as controls.

Sample collection and laboratory preparation

In the summer of 2007, we collected mineral soils from within each of two control and limed subcatchments. The forest floor was first removed by placing a 15 cm x 15 cm wood frame on the surface of the Oe horizon and cutting out a block of OM using a knife. All forest floor material was removed, either as an intact block, or by hand and with a spoon. The forest floor-mineral soil interface was typically easy to identify due to the presence of an E horizon immediately below the Oa horizon. A spoon was used to remove as much organic matter as possible from this E-Oa boundary, with care taken to minimize mixing of mineral and organic horizons. Once the forest floor was removed, mineral soils were sampled incrementally for depths 0 - 10 cm, 10 - 20 cm, 20 - 30 cm, and 30 - 40 cm using a diamond-tipped rotary coring device with 9.5 cm internal diameter (Rau et al. 2011).

In the laboratory, soil samples were dried at 50^{o} C, then passed through a 2 mm sieve. Composite soil samples for each subcatchment were made by mixing equal amounts of soil from all sampled locations, for each sampled depth (n = 25 cores per depth, per subcatchment). For

our sorption analysis, we combined soils sampled from the 20 - 30 cm and 30 - 40 cm increments so that our study consisted of 3 mineral soil depths: 0 - 10 cm, 10 - 20 cm, and 20 - 40 cm. In the summer of 2008, 15 cm x 15 cm blocks of Oe and Oa forest floor horizons were collected from the same 5 plots per subcatchment sampled for mineral soils the previous year. Samples were kept cool until being sieved in the laboratory, with Oe and Oa layers being passed through 5.6 mm and 4 mm sieves, respectively. Soluble organic matter was then extracted by adding 200 mL of deionized water to 20 g of field moist material. The soil-water slurry was shaken for 24 hours on a shaker table and filtered through an ashed glass fiber filter. Extracts were then frozen until the sorption experiment in April, 2009. After thawing, stock solutions of control and limed plot DOM were generated by combining the Oe and Oa extracts from the two control and two limed subcatchments, respectively. The composite DOM solutions were filtered through an ashed glass fiber filter to remove DOM that had flocculated during freezing.

Soil characterization

Three replicates of each composite mineral soil sample were analyzed for total C and N content, exchangeable Ca, and soil pH. For C and N analysis, samples were ground to a fine powder using a Retsch Mixer Mill, type MM200 and combusted using a Vario EL III elemental analyzer. Soil exchangeable Ca was extracted by mixing 100 mL of 1 *M* ammonium chloride with 10 g of soil and placing the solution on a shaker table for 1 hour. Following shaking, the solution was filtered via vacuum filtration through a Pall brand type A/E glass fiber filter. Samples were then frozen until analysis using inductively coupled plasma emission spectroscopy at the State University of New York College of Environmental Science and Forestry. Soil pH was measured using an Accumet basic AB15 pH meter with a flushable junction soil probe, after

mixing a 10 g subsample of soil with 20 mL of deionized water. Following a 30-minute equilibration, samples were gently swirled and a reading was taken after pH stabilized.

DOM characterization and sorption experiment

Using the limed and control DOM stock solutions, we performed a serial dilution to generate 6 DOM concentrations that were 0, 20, 40, 60, 80, and 100% of the initial stock solution for each DOM type. Five mL of 1*M* sodium chloride (0.01*M* final concentration) were added to each solution to maintain a consistent ionic strength. Subsamples of all stock solutions were analyzed for DOC and total dissolved N (TDN) on a Shimadzu TOC-V CPN total organic carbon analyzer. Ammonium (NH_4^+) and nitrate (NO_3^-) were measured on an additional subsample on an autoanalyzer (Perstorp Analytical 500 Series Flow-injection) at the University of Washington College of Forest Resources Analytical Services Center. Dissolved organic N was calculated by subtracting the sum of NH_4^+ and NO_3^- from TDN. Stock solution anion concentrations were quantified using a Dionex ICS-2000 ion chromatograph.

Sorption experiment

We conducted batch equilibration experiments using the 6 concentrations of DOM and 3 soil-DOM combinations: DOM originating in control plots added to soil from control plots ($DOM_{Control}Soil_{Control}$), DOM from control plots added to limed soil ($DOM_{Control}Soil_{Limed}$), and DOM from limed plots added to limed soil ($DOM_{Limed}Soil_{Limed}$). These combinations were then applied to the three soil depth increments (0 - 10 cm, 10 - 20 cm, 20 - 40 cm), and each of the 6 DOM concentrations. Two replicates of each soil-DOM-depth combination were included in the batch equilibration.

For the batch equilibration, 4 grams of dried soil were combined with 40 mL of DOM solution in a 280 mL plastic container. The DOM-soil slurry was shaken for 24 hours, then vacuum filtered through an ashed glass fiber filter. Subsamples of all soil extracts were analyzed for DOC and DON using the same methods described above for the stock solutions.

To evaluate the sorption dynamics between soil and DOM, we constructed linear mass isotherms for each soil-DOM combination and soil depth increment. The initial mass isotherm approach accounts for native DOM sorbed to soil surfaces and has been shown to generate a linear relationship between initial DOC concentrations and the relative retention of DOC and DON in soils high in DOM (Nodvin et al. 1986, Vandenbruwane et al. 2007). Initial mass isotherms display the relationship between the initial DOC and DON concentration of solution added to the soil and the difference between this initial concentration and the concentration in solution at the end of the equilibration period. Here, we display values of DOC and DON retention and loss that have been standardized for total soil C and N concentrations, to account for heterogeneity across our field site. Negative differences indicate net release of DOC or DON from the soil surface into solution and positive differences indicate a net retention of DOC or DON by the soil.

Statistics

Statistical analysis was performed using JMP 7.0 (SAS Institute). Analysis of co-variance was used to determine statistically significant differences among treatments while accounting for differences in isotherm slopes. The analysis measured overall effects between the $DOM_{Control}Soil_{Control}$ treatment relative to the $DOM_{Control}Soil_{Limed}$ and $DOM_{Limed}Soil_{Limed}$

treatments. After confirming main effects, mean comparisons were made using Tukey's test ($p < 0.05$).

RESULTS

Soil and initial DOM characterization

The control soils had higher concentrations of C and N and a lower C:N ratio than limed soils for all soil depth increments (Table 2.1). Exchangeable Ca concentrations in limed soils averaged 216%, 127%, and 86% higher than controls for the 0 - 10 cm and 10 - 20 cm, and 20 - 40 cm depth increment, respectively. Soil pH varied little between the treatment and control. The DOM composite stock solution generated from control soils contained slightly higher DOC than that originating in limed soils (35.4 mg L^{-1} versus 32.4 mg L^{-1}) and similar DON concentrations (Table 2.2). The relatively higher DOC content in control DOM resulted in a higher DOC:DON ratio for control DOM relative to limed (20.1 versus 17.2). The pH of the stock solution containing DOM from limed plots was higher than that of controls (7.5 and 5.3, respectively; Table 2.2). The control DOM stock solution contained slightly higher chloride and NO_3^- and slightly lower SO_4^{2-} and phosphate concentrations than limed DOM (Table 2.2).

For the DOC initial mass isotherms, the 0 - 10 cm and 10 - 20 cm depth increments exhibited a net release of DOC into solution for all soil-DOM combinations, and at all six initial DOC concentrations (Figure 2.1A and B). DOC release declined with soil depth for all treatments. With the exception of the $DOM_{Control}Soil_{Control}$ combination, higher initial DOC concentration in the added DOM solution correlated with reduced net release for all treatments at all depths, as indicated by positive slopes of the isotherms. The $DOM_{Control}Soil_{Control}$ combination showed no change in retention in the 0 - 10 cm depth, regardless of the amount of initial DOC

Table 2.1. Soil properties of limed and control composite mineral soil samples. Mean values reported ± SE (n = 2 subcatchments).

		Soil depth		
Soil origin		0 - 10 cm	10 - 20 cm	20 - 40 cm
Control	C (%)	6.6 ± 1.7	6.6 ± 1.3	5.2 ± 1.1
Limed		5.4 ± 0.5	5.6 ± 0.3	3.5 ± 0.4
Control	N (%)	0.32 ± 0.08	0.28 ± 0.06	0.21 ± 0.04
Limed		0.22 ± 0.03	0.21 ± 0.02	0.13 ± 0.01
Control	C:N ratio	21.4 ± 0.19	23.9 ± 0.60	24.8 ± 0.32
Limed		24.4 ± 0.85	26.4 ± 1.15	27.5 ± 0.96
Control	Exchangeable Ca	0.57 ± 0.17	0.33 ± 0.09	0.22 ± 0.04
Limed	($cmol_c\ kg^{-1}$ soil)	1.8 ± 0.21	0.75 ± 0.11	0.41 ± 0.04
Control	pH	3.9 ± 0.09	4.2 ± 0.0	4.4 ± 0.09
Limed		4.1 ± 0.21	4.2 ± 0.1	4.5 ± 0.09

Table 2.2. Control and limed composite DOM stock solution pH and concentrations of DOC, DON, and anions. Values are from composite stock solution samples.

	DOM origin	
	Control	Limed
DOC (mg L^{-1})	35.4	32.4
DON (mg L^{-1})	1.8	1.9
DOC:DON ratio	20.1	17.2
pH	7.5	5.3
Anions		
Cl^-	0.9	0.6
SO_4^{2-}	1.4	2.0
NO_3^-	0.9	0.6
PO_4^{3-}	0.05	0.16

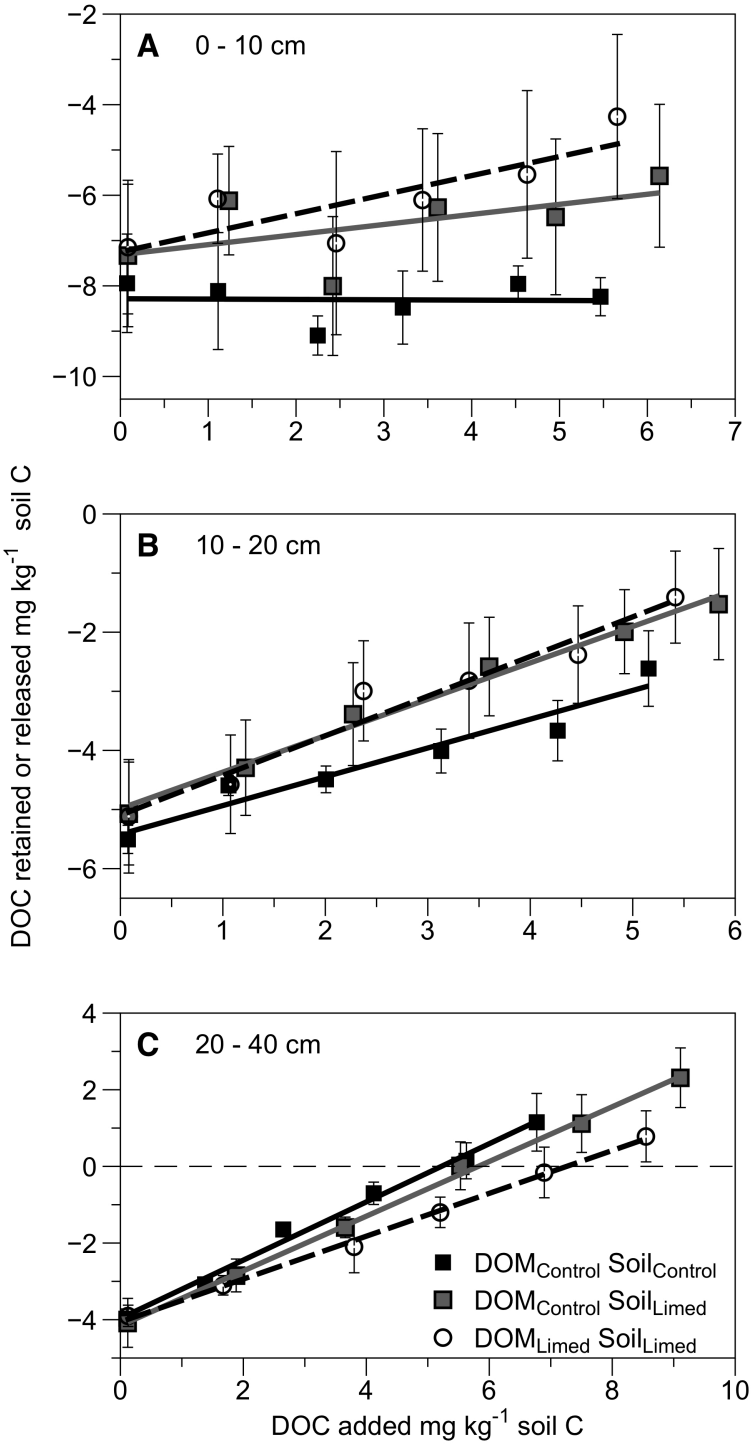

Figure 2.1. Initial mass isotherms for DOC for each soil-DOM combination at 0 - 10 cm, 10 - 20 cm, and 20 - 40 mineral soil depth increments. Error bars indicate ± SE (n = 2 subcatchments).

added. Within the 0 - 10 cm depth increment, the $DOM_{Control}Soil_{Control}$ combination showed a significantly larger net DOC release than the $DOM_{Limed}Soil_{Limed}$ treatment ($P = 0.04$) and did not differ from $DOM_{Control}Soil_{Limed}$ ($P = 0.45$). No significant differences were observed among treatments at 10 - 20 cm depth. The two treatments containing limed soil did not differ significantly from one another at either 0 - 10 cm and 10 - 20 cm depths. At 20 - 40 cm depth, net retention of DOC was observed for the highest initial DOC concentration for the $DOM_{Control}Soil_{Control}$ and $DOM_{Limed}Soil_{Limed}$ treatments (mean added DOC concentrations were 5.0 and 7.0 DOC - C kg^{-1} soil C, respectively; Figure 2.1C). For the $DOM_{Control}Soil_{Limed}$ treatment, mean initial DOC concentrations above 6.0 DOC - C kg^{-1} soil C exhibited net DOC retention. At this depth $DOM_{Control}Soil_{Control}$ differed significantly from $DOM_{Limed}Soil_{Limed}$ ($P < 0.0001$), displaying a relatively smaller net DOC release at lower initial added DOC concentrations and relatively greater retention at initial DOM concentrations where retention was observed.

Initial mass isotherms for DON revealed a net release of DON for all treatments and initial added concentrations, for all studied depths (Figure 2.2). Similar to DOC, the net release of DON tended to decrease as the concentration of DON added increased, as indicated by the positive isotherm slopes. There were exceptions however, including $DOM_{Control}Soil_{Limed}$ samples in the 0 - 10 cm increment, which showed a slight decrease in retention with increasing DON added, and $DOM_{Control}Soil_{Control}$, which exhibited increased DON release with higher initial added DON at both 0 - 10 cm and 10 - 20 cm depth. The $DOM_{Control}Soil_{Control}$ combination was significantly different from $DOM_{Limed}Soil_{Limed}$ at 0 - 10 cm ($P < 0.0001$) and from both $DOM_{Limed}Soil_{Limed}$ and $DOM_{Control}Soil_{Limed}$ in the 10 - 20 cm depth increment ($P = 0.01$ and 0.05, respectively). No significant treatment differences were observed at 20 - 40 cm depth. The two

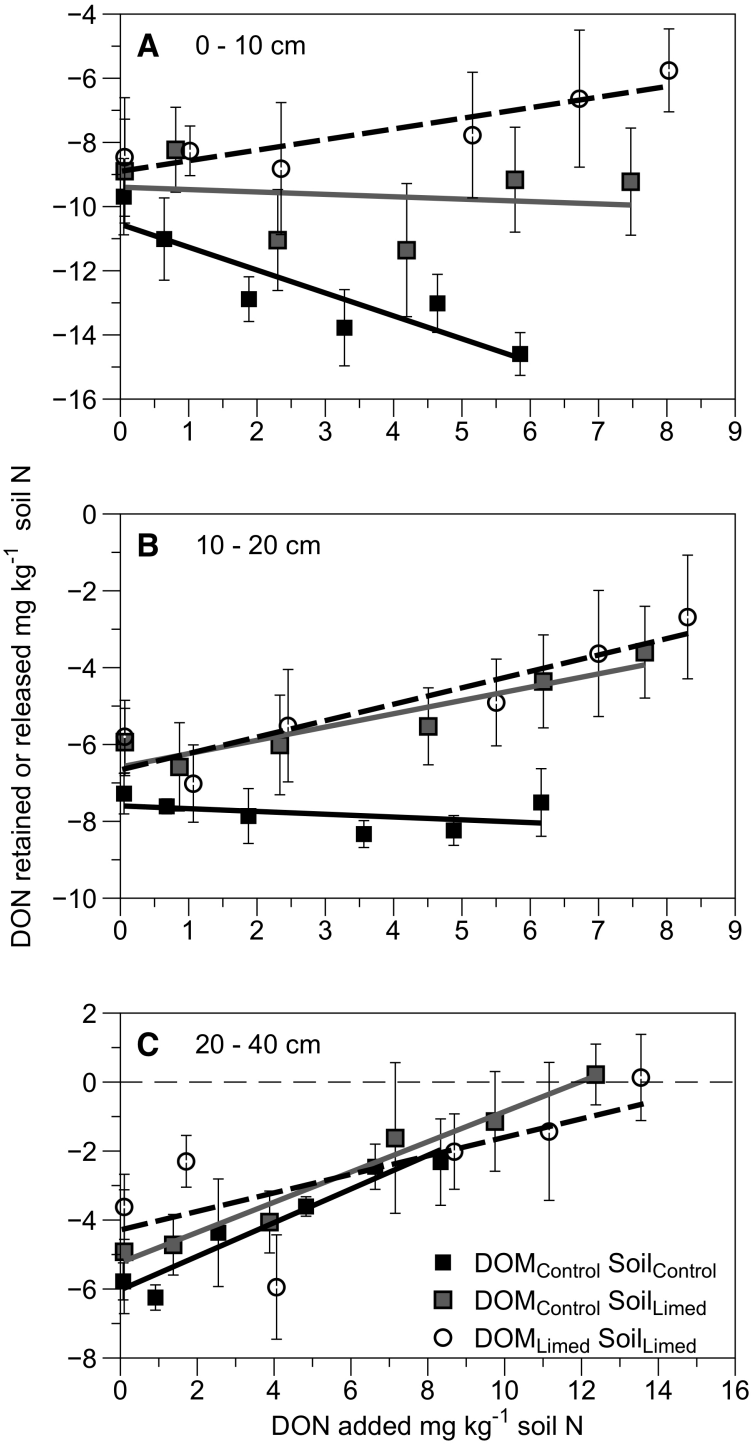

Figure 2.2. Initial mass isotherms for DON for each soil-DOM combination and studied depth increment. Error bars indicate ± SE (n = 2 subcatchments).

treatments containing limed soil did not differ significantly from one another for any studied depth.

DOC concentrations in the equilibrated solution generally increased linearly with increasing initial added DOC concentration. Final DOC concentrations were highest in the 0 - 10 cm soil depth increment and lowest at 20 - 40 cm depth for all treatments (Table 2.3). For all depths, final concentrations were highest in $DOM_{Control}Soil_{Control}$, intermediate for $DOM_{Control}Soil_{Limed}$ and lowest for the $DOM_{Limed}Soil_{Limed}$ treatment. Final solution DOC concentrations ranged from 15.1 mg L^{-1} (in the $DOM_{Limed}Soil_{Limed}$ treatment, at 20 - 40 cm depth, with 0% initial DOC added), to 94.5 mg L^{-1} ($DOM_{Control}Soil_{Control}$ treatment, 0 - 10 cm depth, with 100% stock solution). A similar pattern in depths and among treatments was observed for DON, with final DON values ranging from 0.5 to 6.7 mg L^{-1} (Table 2.3).

The mean DOC:DON ratio of the final solution was lower than that of the initial added DOM solution for all $DOM_{Control}Soil_{Control}$ and most $DOM_{Control}Soil_{Limed}$ treatments for all depths and initial DOM concentrations (Figure 2.3). The DOC:DON ratio of the final solution tended to decrease with increasing initial added DOM concentration, resulting in a greater difference between initial and final DOC:DON values. In contrast, most $DOM_{Limed}Soil_{Limed}$ samples exhibited higher DOC:DON ratios in the final solution relative to initial limed DOM. The final DOC:DON values were similar among all treatments, despite the different DOC:DON ratio of the added solution in the $DOM_{Limed}Soil_{Limed}$ samples.

DISCUSSION

In acid-impacted forests, changes in soil pH and Ca availability have the potential to influence ecosystem DOC and DON dynamics. When management strategies, such as liming, are

Table 2.3. DOC and DON concentrations (mg L^{-1}) in the final solution of samples equilibrated with the lowest (0%) and highest (100%) DOM concentrations. Initial added concentrations for the 100 % stock solutions are listed in Table 2.2.

	Treatment		
Stock solution	$DOM_{Control}Soil_{Control}$	$DOM_{Control}Soil_{Limed}$	$DOM_{Limed}Soil_{Limed}$
DOC			
0 - 10 cm			
0 %	52.0	39.0	37.9
100 %	94.5	66.7	55.8
10 - 20 cm			
0 %	36.9	28.5	28.5
100 %	55.3	44.3	40.6
20 - 40 cm			
0 %	20.6	17.1	15.1
100 %	30.3	26.7	29.7
DON			
0 - 10 cm			
0 %	3.0	1.9	1.8
100 %	6.7	3.9	3.2
10 - 20 cm			
0 %	2.1	1.3	1.2
100 %	4.1	2.6	2.5
20 - 40 cm			
0 %	1.2	0.7	0.5
100 %	2.3	1.7	1.9

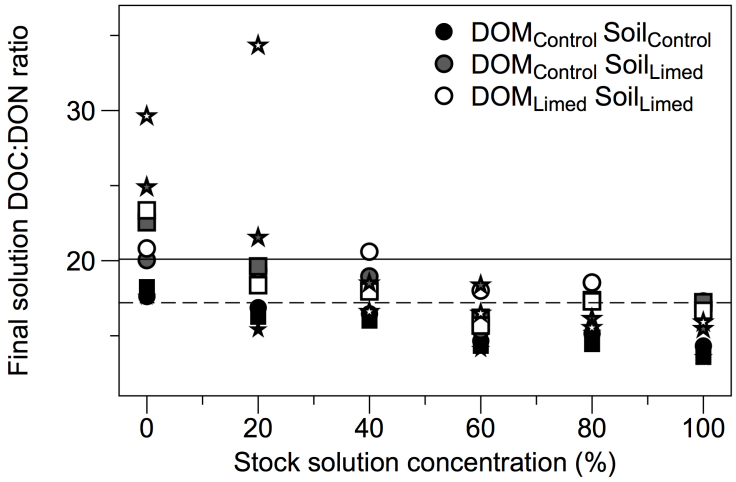

Figure 2.3. DOC:DON ratio of equilibrated solution for each treatment, depth, and concentration of initial added DOM. Different colors represent the 3 treatments (see figure legend) and shapes indicate soil depths (circle = 0 - 10 cm, square = 10 - 20 cm, star = 20 - 40 cm). Horizontal lines indicate the DOC:DON ratio of the initial stock solution (solid line = control DOM, dashed line = limed DOM).

used to mitigate soil acidification, soil properties can be altered. Our results suggest that liming may contribute to reduced DOC and DON losses from the upper mineral soils. We hypothesized that liming would lead to greater DOC and DON sorption in treated soils. While we observed net losses of DOC and DON within the upper mineral soils of all treatments, the smaller release from limed soils suggests that liming may have facilitated greater retention of DOC and DON. The limed soils had much higher exchangeable Ca concentrations than controls while soil pH differed little, allowing us to isolate the response to Ca rather than concurrent Ca and pH changes. This suggests that large increases in exchangeable Ca availability may influence DOM retention, possibly by enhancing Ca-OM bridging, as has been documented in laboratory experiments and agricultural soils (Oades 1988, Muneer and Oades 1989, Mikutta et al. 2007).

The similarity in net losses of DOC and DON from limed soils regardless of the origin of the added DOM indicates that sorption was influenced more strongly by the source of the soil than the source of the DOM. Control and limed DOM stock solution chemistry differed most dramatically in pH and exchangeable Ca content. Additional DOM extracts collected at our site showed a 10-fold difference in Ca content in the forest floor Oe horizon and a 6-fold difference in the Oa layer, with the DOM from limed soils exhibiting greater Ca content than controls. Despite these large differences in solution pH and Ca however, our findings give no indication that these differences in solution chemistry have a strong influence on DOC and DON retention in the top 20 cm of mineral soil. Our results indicate slightly less net loss of DOC and DON in the $DOM_{Limed}Soil_{Limed}$ treatment relative to $DOM_{Control}Soil_{Limed}$ in the 0 - 10 cm depth increment, but this difference was not significant. Any potential differences in sorption due to DOM origin may have been masked by the large net release of DOC and DON from these surface mineral soils.

Net effects of liming on DON retention were similar to those of DOC for the $DOM_{Limed}Soil_{Limed}$ and $DOM_{Control}Soil_{Limed}$ treatments at all soil depths. However, not all treatments showed consistent responses in both DOC and DON to increased initial DOM concentrations. For $DOM_{Control}Soil_{Control}$ samples in the 10 - 20 cm depth increment, higher DOM concentrations resulted in reduced loss of DOC and increased loss of DON. A similar, but less pronounced pattern was also evident at 0 - 10 cm soil depth for this soil-DOM combination. These findings indicate that the controls on DON and DOC retention in unlimed soils may differ, perhaps as a result of differences in the composition of the DOM that we did not measure. Correlations between DOC and DON leaching have been observed (Michalzik et al. 2001), however differences in the movement and retention of these nutrients within the soil profile can occur if OM fractions with differing DOC:DON ratios are preferentially mobilized or removed as a result of liming or differences in C and N mineralization rates (Andersson et al. 1999, Andersson et al. 2000).

The DOC:DON ratio of the equilibrated solution was typically lower than that of the initial added solution and decreased with increasing initial added DOM concentration. For the $DOM_{Control}Soil_{Control}$ samples in the 0 - 10 cm and 10 - 20 cm depths, the greater DON release with increasing initial DOM concentration could have contributed to this pattern. This is unlikely to be the dominant factor however, because the decreased ratio was observed in all treatments. The change in DOC:DON ratio between initial and final solutions indicate that the composition of the added DOM differs from that of the DOM released from the soil. These could be caused by changes in DOM chemistry that occur between the forest floor (our DOM source) and the mineral soil. In the forest floor, preferential mineralization of more labile compounds (with a higher DOC:DON ratio) by the microbial community within the forest floor could lead to

proportionally larger fractions of recalcitrant materials leaching into the mineral soils (Qualls et al. 2002), which is measured in our post-equilibration samples. Additionally, the composition of DOM can affect the solution DOC:DON ratio and retention. Hydrophobic acids sorb more strongly to soil surfaces than hydrophilic compounds and also tend to have larger DOC:DON ratios resulting from lower N contents (Qualls and Haines 1992, Kaiser and Guggenberger 2000, Nilsson et al. 2001). If the added DOM had a high proportion of hydrophobic acids, this could have displaced hydrophilic acids that may have been previously sorbed, allowing for a release of N-rich DOM, which could contribute to the observed decrease in DOC:DON ratio. Interestingly, at high initial added DOM concentrations the DOC:DON ratio of the final solution differed little between the lime and control treatments. This suggests that the composition of the native DOM residing in limed and control soils may be similar despite observed differences in DOC and DON retention, soil exchangeable Ca availability, and solution chemistry.

The large net losses of DOC and DON observed in all treatments in the 0 - 10 cm and 10 - 20 cm depth increments were likely due to high concentrations of native DOM in the soil. The forest floor at this site is very large, with mean C and N stocks of 49 and 2 tons ha^{-1}, respectively (Chapter 3) and the forest floor is typically the greatest source of DOM to mineral soils (Qualls et al. 2002). High production of DOM in the forest floor could increase the quantity of native DOM within the mineral soil via leaching, which could then lead to inhibition of additional DOM sorption (Jardine et al. 1989). It has also been shown that soils may become saturated with C and are unable to retain additional C inputs once saturation is reached (Stewart et al. 2007). Other studies have documented net losses of DOC from shallow mineral horizons in spodosols at similar initial added DOC concentrations (Ussiri and Johnson 2004). Our results suggest that liming can reduce DOM losses, however the pattern of greater DOC and DON release from

control soils containing inherently greater C and N concentrations indicate that further work is needed to confirm treatment effects. Since large quantities of OM in soil can hinder further retention, (Jardine et al. 1989, Kaiser et al. 1996, Kaiser and Zech 2000, Kothawala et al. 2009), it is possible that the pattern of greater DOC and DON release in control soils that we observed was influenced by relatively higher soil C and N concentrations than was present in limed soils. However, we standardized our values in the isotherms to account for soil C concentrations and still observed a significant difference in DOM release between control and limed treatments in the 0 - 10 cm depth increment.

While batch equilibration experiments can provide important insights into patterns of DOM sorption, it is difficult to discern whether this method can effectively capture natural soil processes and explain ecosystem-scale responses to changes in soil acidification or liming. The large losses of DOC and DON we observed could have been an artifact of the use of soils that had been dried and sieved prior to equilibration - both standard procedures. These processes disrupt aggregate structure and may have increased the quantity of exposed OM, which could result in an overestimate of what DOC and DON release compared to *in situ* conditions. The composition of the DOM we added was also likely altered by our methods. Stock solution DOM samples were frozen prior to our experiment which resulted in OM flocculation that may have preferentially removed one or more OM fractions. Further, the concentrations and composition of the added DOM differ from that in the natural ecosystem. Prior research at Woods Lake found DOC concentrations to be 12-15 mg L^{-1} in zero tension lysimeters installed just below the Oa horizon (Geary and Driscoll 1996). These values are equivalent to those found in our initial added concentration that was 40% of the stock solution, indicating that half of our initial added concentrations may have been above what would leach into the mineral soil in the field. We saw

the largest net release at the lower initial DOC and DON concentrations, suggesting that ecosystem-scale losses of DOM from the upper mineral soils could be quite large.

The movement and retention of DOC and DON within forest soils is an extremely complex process. In ecosystems exposed to high acid deposition, changes in soil pH and exchangeable Ca availability can alter C and N cycling and retention. While observational research now links increased DOC and DON concentrations in surface waters to reduced acid inputs (Evans et al. 2006, Monteith et al. 2007), the impacts of soil liming on DOC and DON retention remain unclear. Our data suggest that increasing exchangeable Ca availability in soils may reduce DOC and DON losses. Further research investigating changes in the composition of DOM and sorption in deeper soil horizons could provide important insights into the mechanisms controlling DOC and DON retention, the nature of organo-mineral interactions, and how management strategies such as liming affect ecosystem C and N balance.

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CHAPTER 3

Forest liming increases forest floor C and N stocks in a mixed hardwood forest

ABSTRACT

We investigated the effects of forest liming on above- and belowground carbon (C) and nitrogen (N) pools and fluxes in the Woods Lake Watershed, Adirondack Park NY. In 1989, 6.89 t ha^{-1} of calcium carbonate ($CaCO_3$) was applied to two subcatchments within this watershed to mitigate the effects of acid deposition, while two additional subcatchments were retained as controls. Eighteen years after liming, soil pH and exchangeable calcium (Ca) pools remain elevated in the forest floor and upper mineral soil of the limed plots. Forest floor C and N stocks were significantly larger in limed plots (68 vs. 31 t ha^{-1} C, and 3.0 vs. 1.5 t ha^{-1} N) and were driven primarily by greater accumulation of Oa material. Liming reduced basal soil respiration rates by 17 and 43% in the Oe and Oa forest floor horizons, respectively. Net N mineralization was significantly lower in the limed soils for both forest floor horizons and nitrification was enhanced in the Oe layer. Mineral soil C and N stocks were more variable, but do not appear to be largely affected by liming. Aboveground, there was a net decline in live tree biomass across the entire watershed and no liming effect was evident. Both forest floor fine root and foliar litter C inputs were larger in limed plots, but this difference was statistically significant only for roots in the Oe horizon. Liming has altered ecosystem-scale C and N balances at this site, driven largely by a suppression of decomposition in the forest floor and increased organic matter inputs in limed plots. These results emphasize the need to improve our understanding of the effects of liming on hardwood forests, the interactions among Ca, C, and N cycles, and the long-term impacts of acid deposition on forest C and N uptake and retention.

INTRODUCTION

Nutrient availability in northeastern U.S. forests has been dramatically altered by anthropogenic activities. Acid deposition has increased nitrogen (N) availability and forest growth, but has also been linked to soil acidification, base cation losses, and declines in some temperate tree species (Siccama et al. 1982, van Breemen et al. 1983, Likens et al. 1996, Driscoll et al. 2001, Thomas et al. 2010). Amendments to the Clean Air Act have reduced the deposition of sulfate, a strong acid anion; however, N deposition remains high (NADP 2008) and declines in soil pH and exchangeable base cations, especially calcium (Ca), are continuing throughout the region (Bailey et al. 2005, Johnson et al. 2008, Warby et al. 2009). Calcium is typically the most abundant base cation on the soil exchange complex and is important in neutralizing acids in soil (Likens et al. 1998, Driscoll et al. 2001). As a result of this important function, studies of Ca cycling have focused largely on the links between Ca and acidification, including how Ca availability affects soil pH, mobilization of aluminum (Al), and the acid neutralizing capacity of freshwaters (Cronan and Schofield 1990, Driscoll et al. 2001). Far fewer studies have investigated how altered soil Ca content and changes in pH influence forest carbon (C) sequestration.

Calcium has many roles in forest ecosystems that can directly affect C and N stocks and fluxes. Trees utilize Ca for numerous biological functions that dictate C and N uptake and storage in tissues. These processes include growth, stomatal regulation, carbohydrate metabolism, cell wall synthesis and structure, and response to environmental stress (McLaughlin and Wimmer 1999, Lautner and Fromm 2010). Changes in pH and soil Ca content can also influence microbial and faunal communities, with higher Ca availability and soil pH often

leading to increased microbial activity (Haimi and Huhta 1990), higher earthworm abundance, and higher rates of litter decomposition (Reich et al. 2005, Hobbie et al. 2006). In contrast, Ca can reduce the mobility and solubility of dissolved organic matter (OM) in mineral soils by forming cation bridges which stabilize OM and reduce decomposition, leading to greater OM retention (Tipping and Ohnstad 1984, Muneer and Oades 1989, Romkens et al. 1996, Chan and Heenan 1999, Oste et al. 2002, Mikutta et al. 2007). More recent work has also demonstrated that increased Ca availability can lead to greater N uptake by plants and reduced microbial N cycling, thereby reducing potential ecosystem N losses via leaching (Groffman and Fisk 2011).

Forest liming (with $CaCO_3$) has been used as a management strategy to reduce the effects of acidification and often leads to increased soil pH and exchangeable Ca concentrations. Liming studies provide an opportunity to explore interactions among C, N, and Ca cycles, as well as identify how this management technique affects ecosystem nutrient availability. Liming has been conducted extensively across Europe in conifer plantations and in some northeastern U.S. forests dominated by sugar maple (*Acer saccharum*), a species known to respond positively to increased soil Ca availability (Long et al. 1997, Juice et al. 2006, Huggett et al. 2007). It is unknown whether results of these studies can accurately represent the response of acid-impacted mixed hardwood forests. Further, many studies measure changes in vegetation and soil C and N pools for just a few years immediately following Ca addition, or measure fluxes, such as soil respiration, N mineralization, nitrification, or dissolved organic C and N leaching, for weeks to months, which may be inadequate to assess long-term impacts of altered soil Ca and pH on ecosystem C and N dynamics.

Here, we investigate changes in C and N pools and fluxes approximately 20 years after an experimental Ca addition in the Woods Lake Watershed, a mixed northern hardwood forest

located in the Adirondack Park, NY. In 1989, lime was added to roughly half of the catchment area to assess whether forest liming could be an effective strategy to reduce acidification of surface waters (Driscoll et al. 1996). We hypothesized that the lime addition would improve forest health and that this improvement would be evident in increased tree biomass, leaf litter, and fine root production. Within the forest floor, we anticipated that the increased pH associated with liming would stimulate microbial activity resulting in increased decomposition, basal soil respiration, and net N mineralization. We expected enhanced decomposition to lead to reduced C and N stocks in limed forest floor horizons relative to controls. Conversely, we hypothesized that increased Ca availability could enhance Ca-OM complexation in the upper mineral soils, leading to increased C and N stocks in these horizons.

METHODS

Site Description

Research was conducted in the Woods Lake Watershed, the site of an Experimental Watershed Liming Study, located in Herkimer County NY, within the Adirondack Park (43^{o} 52' N, 74^{o} 57' W). In 1989, limestone was applied by helicopter to two ~50 ha subcatchments (L1 and L2) in a single application of 6.89 tons $CaCO_3$ ha^{-1} (2.76 t Ca ha^{-1}) (Driscoll et al. 1996). The lime pellet was 82% $CaCO_3$, 8% $MgCO_3$ and 4% organic binder (Driscoll et al. 1996). Two additional subcatchments were maintained as controls (C1 and C2). Mean annual precipitation at this site is 1230 mm and mean annual temperature is 5.2^{o}C (Yavitt et al. 1995).

This watershed has 98% forest cover (Staubitz and Zarriello 1989) and is dominated by American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), and yellow birch (*Betula alleghaniensis*), with lesser amounts of red spruce (*Picea rubens*), sugar maple (*Acer*

saccharum), and striped maple (*Acer pensylvanicum*) (Smallidge and Leopold 1994)(Appendix 3A, Table 3.2A). The site is underlain by hornblende granitic gneiss bedrock covered by a sandy glacial till comprised of quartz and feldspar, with some interspersed hornblende, ilmenite and magnetite (April and Newton 1985). The soils are classified as Orthod Spodosols (Smallidge and Leopold 1994) and mean mineral soil depth is 30 to 35 cm (Brocksen et al. 1988). Calcium is the dominant base cation in these soils (Blette and Newton 1996). Within 1-2 years after liming, the pH in the forest floor rose from 3.7 to 4.9 in the Oe horizon and from 3.7 to 4.0 in the Oa (Simmons et al. 1996). Exchangeable Ca availability also increased during this period, from 8.5 to 35 $cmol_c\ kg^{-1}$ soil in the Oe and from 6 to 10 $cmol_c\ kg^{-1}$ soil in the Oa (Blette and Newton 1996). Following these early studies, very little research has been conducted within the forest at this site.

Plot design

Vegetation and soil sampling was conducted in twenty 0.04 ha plots from across the watershed, distributed as 5 plots located along transects spanning each of the limed and control subcatchments (Appendix 3A). These plots were a subset of the 99 plots established during the original vegetation sampling in 1989 (Smallidge and Leopold 1994). All trees ≥ 10 cm diameter at breast height (dbh) were tagged in 1989 and dbh was recorded (P. Smallidge, personal communication). We selected plots for our study to span the spatial heterogeneity of the landscape and to minimize differences in tree species composition, slope, and aspect between control and limed subcatchments.

Aboveground vegetation measurements

In August 2009, dbh was measured on all trees ≥ 10 cm within each study plot. Aboveground tree biomass was calculated using allometric equations from Jenkins et al. (2003). To convert to units of C, we assumed that woody biomass is 50% C. Plot mortality and changes in aboveground live biomass were calculated using newly collected data from 2009 and prior measurements from 1989. Litterfall was collected from May 2009 to May 2010 using five 0.23 m^2 (40.6 cm x 55.9 cm) litter baskets distributed across each plot. Baskets were secured in place with stakes and lined with fiberglass window screen to prevent litter material from resting on the bottom of the basket.

Litter was air dried, then sorted into components including: foliage (sorted by species), seeds, branches and wood, and miscellaneous components (e.g. insects). Sorted samples were then dried at 50^{o}C for at least 3 days and weighed. Foliar litter from all baskets within a plot was combined by tree species into one composite sample per plot for analysis of C, N, Ca, and lignin. The composite foliage samples were ground to a fine powder using a Cyclone Sample Mill (Udy Corp., Fort Collins CO). Total C and N concentrations were measured via high temperature combustion using a Vario EL III elemental analyzer (Elementar, Hanau Germany) at Cornell University. Total Ca concentration was analyzed by nitric acid microwave digestion followed by analysis using a Varian Vista AX inductively coupled plasma atomic emission spectrometer at the U.S. Forest Service Laboratory, Durham NH. Foliar litter lignin content was determined at the Dairy One Forage Laboratory, Ithaca NY. Samples were digested in an ANKOM A200 fiber analyzer using the ANKOM A200 filter bag technique. First, samples were placed in filter bags and submerged in acid detergent fiber solution for 75 minutes in an ANKOM A200 Digestion Unit. Samples were then rinsed in boiling water, then in acetone, before being dried at 100^{o}C for

two hours. The remaining residue was combined with 72 % sulfuric acid for 3 hours in an ANKOM A200 DaisyII Incubator. Lignin concentration was then determined using a FOSS NIRSystems Model 6500 VIS-NIR Spectrometer.

Soil field measurements

As detailed below, forest floor material was sampled on several occasions for various analyses. Forest floor mass was assessed twice on the 20 intensively studied plots, first in 2007 when both Oe and Oa were collected as a single sample, and again in 2008, when Oe and Oa were collected separately. All forest floor chemistry and mass data presented here is from the 2008 sample collection. During 2010, additional forest floor material was collected incrementally by horizon in the sample plots for measurement of soil basal respiration. Forest floor depth was also characterized at 100 additional locations within each subcatchment to assess watershed-wide forest floor depth patterns.

In the summer of 2007, forest floor and mineral soils were collected from 5 locations within each of the 20 study plots. The forest floor was collected by placing a 15 cm x 15 cm wood frame on the surface of the Oe and cutting out a block of OM using a knife. Roots within the block were clipped with pruners at the edges of the frame and all forest floor material was removed, either as an intact block, or by hand and with a spoon. After removal of the block, forest floor depth was recorded. The interface between the forest floor and mineral soil was usually easy to identify due to the presence of an E horizon immediately below the Oa. A spoon was used to collect as much OM as possible from this E-Oa boundary, with care taken to minimize mixing of mineral and organic horizons. Mineral soils were sampled incrementally for depths 0 - 10 cm, 10 - 20 cm, 20 - 30 cm, and 30 - 40 cm using a diamond-tipped rotary coring

device with 9.5 cm internal diameter, which provides a quantitative sample of soil bulk density and OM stocks (Rau et al. 2011). Collected mineral soil samples were used to quantify current soil pH, exchangeable Ca availability, and C and N stocks.

In 2008, additional forest floor samples were collected from six locations within each plot to quantify forest floor pH, exchangeable Ca pools, C and N stocks, and net N mineralization. The 2007 sampling revealed differences in forest floor mass between limed and control plots. To further explore this pattern and improve the resolution of our forest floor analyses, we collected Oe and Oa horizons separately in 2008. Similar to the 2007 sampling, we used a knife to cut out 15 cm x 15 cm blocks. We first removed the Oe layer. This layer consisted of partially fragmented litter, had a light brown color, and typically was removed as a solid block held together by hyphae and roots. The Oa horizon was dark brown to black in color, very moist, and often had to be removed with spoons and by hand.

An *in situ* net N mineralization study was conducted during the 2008 sampling and included the Oe and Oa samples described above, as well the top 10 cm of mineral soil. At each of the six sampling locations, 2 samples of Oe, Oa, and 0 - 10 cm mineral soil were taken side-by-side. Mineral soil was collected using a tulip bulb corer (7 cm diameter). One set of samples (initial) was kept on ice packs and returned to the laboratory shortly after collection. These initial Oe and Oa samples were used to quantify forest floor pH, exchangeable Ca availability, C and N stocks, and pools of ammonium (NH_4^+) and nitrate (NO_3^-). The second set of soil samples (incubated) were sealed in polyethylene bags in the field and placed back in the soil from which they were removed. After a 30-day *in situ* incubation, samples were retrieved, placed on ice packs, and returned to the laboratory for analysis. In September 2010, additional Oe and Oa

samples were collected from a 15 cm x 15 cm area using a square-edged shovel. Samples were kept on ice packs during transport and later used to assess basal soil respiration.

We also recognized that our study plots may not adequately represent forest floor dynamics across the entire 200 ha watershed. To investigate this, we took additional forest floor depth measurements in all subcatchments in 2010 (100 measurements across each subcatchment).

Laboratory analyses

The forest floor and mineral soil samples collected in 2007 were dried at 50^{o}C for approximately 1 week. These samples were then weighed, but no chemical analyses were performed. Mineral soils collected in 2007 were passed through a 2 mm sieve and rock and roots were removed and weighed. The Oe and Oa samples collected in 2008 were passed field moist through 5.6 mm and 4 mm sieves, respectively. All roots were removed from these samples while sieving. Large root pieces that slipped through the sieve were retrieved for quantification. Samples were then dried at 50^{o}C for at least 3 days. Forest floor fine root biomass was estimated later on Oe and Oa samples by sorting the dried samples into > 2 mm and < 2 mm size classes, then re-drying and weighing the < 2 mm roots. Two 10 g subsamples of moist Oe and Oa material were collected to determine moisture content and to measure net N mineralization (detailed below). The remaining sample was dried at 50^{o} C for at least 5 days, then 3 additional ~10 g subsamples were removed for analysis of total C, N, exchangeable Ca, and pH.

A subsample of forest floor (2008 collection) and mineral soil (2007 collection) samples were ground to a fine powder using a Retsch Mixer Mill, type MM200, and analyzed for total C and N on a Vario EL III elemental analyzer. Exchangeable cation concentrations were measured

using a 1*M* ammonium chloride (NH_4Cl) extraction. Five grams of forest floor material were combined with 50 mL of NH_4Cl and 10 g of mineral soil were mixed with 100 mL of NH_4Cl. Each sample was placed on a shaker table for 1 hour. After shaking, solutions were vacuum filtered through Pall brand type A/E glass fiber filters. Extracts were frozen until analysis, using inductively coupled plasma emission spectroscopy at the State University of New York College of Environmental Science and Forestry, Syracuse NY. Soil pH analysis was performed using an Accumet basic AB15 pH meter with a flushable junction soil probe. For the mineral soils, a 10 g subsample of soil was mixed thoroughly with 20 mL of deionized water. For forest floor material, 5 g of sample were mixed with 50 mL of water. After a 30-minute equilibration, samples were gently swirled and a reading was taken after pH stabilized.

To assess net N mineralization and nitrification of both initial and incubated Oe, Oa and 0 - 10 cm mineral soil samples, 10 g of field moist soil was mixed with 100 mL of 1*M* KCl and placed on a shaker table for 1 hour. After shaking, samples were passed through a Whatman Type GF/F glass fiber filter via vacuum filtration. Prior to sieving, soil samples were kept refrigerated. All extractions were performed on the same day the sample was sieved, and within 1 week of collection. Extracts were then frozen until analysis using the automated flow injection phenate method on a Lachat QuikChem 8000 automated ion analyzer at the Cary Institute of Ecosystem Studies, Millbrook NY. Net N mineralization was calculated as the difference between the incubated and initial sample concentrations of NH_4^+ and NO_3^- in the paired samples for each depth increment studied. Net nitrification was calculated as the accumulation of NO_3^- between the incubated and initial samples.

To measure soil basal respiration, the 5 samples collected within each plot in 2010 were composited by depth increment during sieving, creating one composite Oe and Oa sample for

each plot. Samples were then kept at 4°C until analysis, ~5 months after collection. Approximately 1 week before measuring basal respiration, four subsamples weighing 20 g each (field moist), of each composite sample were placed in 355 mL Ball® glass jelly jars and left in the dark at 22°C. A 10 g subsample of each composite was dried for at least 24 hours at 110°C to calculate soil moisture content. Basal respiration was measured on 2 occasions approximately 3 weeks apart. Sample moisture was maintained by weighing samples weekly and adding deionized water as needed to return soils to field moisture. The last water addition occurred 1 week prior to the second respiration measurement. Soil basal respiration was measured by capping samples with an air-tight lid and allowing CO_2 to accumulate in the headspace. After 24 hours, 2 mL of headspace was removed using a syringe and immediately injected into an infrared gas analyzer (LI-6200, LI-COR, Lincoln NE). One replicate of each composite sample was incubated a third time and the collected headspace was analyzed for ^{13}C, to determine whether any undissolved lime pellets in the limed forest floor samples had contributed to the measured CO_2 accumulation during the incubation. Following the incubation, approximately 5 g of each sample were ground and analyzed for total C and N concentration using the same forest floor analytical methods described above.

Statistics

Statistical analysis was performed using JMP 7.0 (SAS Institute). A mixed model was constructed, containing treatment (control vs. limed) and subcatchment (C1, C2, L1, L2) nested within treatment as fixed effects. Plot and samples obtained within plots were included as random effects. Main liming effects were confirmed using this model, then subcatchment mean comparisons were made using Tukey's test ($P < 0.05$).

RESULTS

Tree response to liming

In 1989, live tree aboveground biomass averaged 123.4 t C ha^{-1} in study plots (Table 3.1). During the 20-year interval since lime application, there was a net decline in aboveground live tree biomass in all subcatchments, averaging 4.5 t C ha^{-1} yr^{-1} and resulting in a mean biomass of 82.3 t C ha^{-1} in 2009. There were no significant differences in biomass loss between limed and control subcatchments. Stand mortality rates, as well as mortality of individual species, did not differ significantly between limed and control areas (Table 3.2). Rates of mortality differed among species, however, with American beech showing significantly greater declines than all other species across the watershed ($P < 0.05$), accounting for 44% of all mortality.

Liming did not affect total annual aboveground litter inputs, nor did it influence any of the measured litter components (Table 3.3). There was a trend toward larger foliar litter inputs in the limed subcatchments (2.96 vs. 2.76 t OM ha^{-1} yr^{-1}), but this relationship was not statistically significant ($P = 0.36$). All tree species exhibited significantly larger Ca concentrations in foliar litter in limed plots relative to controls (Table 3.4). Total foliar Ca inputs (sum of all species) were also significantly higher in limed soils, while total foliar inputs of C and N did not differ between limed and control plots (Table 3.5). Significantly larger C concentrations were observed in the control plot foliar litter of all species except yellow birch (Table 3.4).

Fine root (< 2mm) biomass in the Oe horizon was significantly larger in the limed sites relative to controls ($P = 0.02$; Table 3.6). This pattern was driven by significantly greater root biomass in the L1 subcatchment relative to all other subcatchments. There was no effect of

Table 3.1. Live tree aboveground biomass (t C ha^{-1}) in 1989 and 2009 for all species in each subcatchment. Mean values are indicated ± SE (n = 5 plots).

	Subcatchment and year							
	C1		C2		L1		L2	
Tree species	1989	2009	1989	2009	1989	2009	1989	2009
Beech	25.8 ± 12.8	18.3 ± 5.7	75.7 ± 15.6	41.2 ± 13.4	36.2 ± 5.9	15.7 ± 3.1	62.8 ± 16.4	12.5 ± 3.0
Red maple	27.9 ± 16.3	26.9 ± 10.1	27.0 ± 6.4	19.7 ± 13.5	25.7 ± 12.3	18.3 ± 5.1	14.5 ±4.5	19.9 ± 7.5
Red spruce	6.9 ± 4.3	5.4 ± 3.0	5.9 ± 5.2	0.9 ± 0.5	10.7 ± 6.6	6.2 ± 2.5	14.6 ± 6.6	4.8 ± 3.3
Striped maple	2.0 ± 1.7	3.1 ± 2.0	0.0	3.9 ± 3.2	2.4 ± 1.5	1.9 ± 1.4	0.2 ± 0.2	1.9 ± 0.7
Sugar maple	17.0 ± 9.3	22.8 ± 14.3	0.8 ± 0.8	1.6 ± 1.6	0.9 ± 0.6	0.7 ± 0.7	2.2 ± 1.0	7.2 ± 3.1
Yellow birch	46.0 ± 32.2	14.9 ± 7.3	7.2 ± 3.1	2.0 ± 1.3	60.6 ± 26.8	64.8 ± 34.2	14.6 ± 7.9	14.5 ± 6.7
Other	5.6 ± 6.0	0.0	0.1 ± 0.1	0.0	0.0	0.0	0.0	0.0
Total	131.5 ± 34.2	91.3 ± 10.6	116.8 ± 12.6	69.3 ± 7.7	136.6 ± 22.5	107.6 ± 29.7	108.8 ± 14.3	60.8 ± 6.0

Table 3.2. Estimated aboveground C loss due to tree mortality between 1989-2009 (t C ha^{-1}) for each studied subcatchment. "-" indicates no mortality of that species (no measurable biomass loss or absence of species within subcatchment). Means values presented ± SE (n = 5 plots). Lime effect P values indicate a significant difference between limed and control subcatchments.

	Subcatchment				Lime effect
Tree species	C1	C2	L1	L2	(P value)
Beech	27.9 ± 13.3	66.5 ± 12.5	33.0 ± 5.8	60.9 ± 16.7	0.99
Red maple	33.7 ± 14.3	20.6 ± 8.5	19.1 ± 10.2	10.3 ± 2.3	0.34
Red spruce	8.3 ± 3.3	9.8 ± 6.5	9.7 ± 5.1	14.5 ± 6.8	0.69
Striped maple	3.5 ± 2.3	-	4.0 ± 1.4	1.0	0.78
Sugar maple	16.7 ± 7.9	-	2.9	15.2 ± 0.5	0.37
Yellow birch	46.8 ± 30.3	8.1 ± 3.3	15.0 ± 3.4	9.6 ± 3.5	0.40

Table 3.3. Total annual aboveground litter inputs (t OM ha^{-1} yr^{-1}) for each studied subcatchment. Means indicated ± SE (n = 5 plots).

Litter component	Subcatchment C1	C2	L1	L2	Lime effect (P value)
Foliage	2.73 ± 0.14	2.78 ± 0.15	2.93 ± 0.37	2.99 ± 0.04	0.36
Bark and Branches	1.36 ± 0.59	0.25 ± 0.07	0.45 ± 0.11	0.34 ± 0.10	0.20
Cones	0.001 ± 0.001	0 ± 0	0.0002 ± 0.0002	0.04 ± 0.04	0.34
Seeds	0.01 ± 0.01	0.02 ± 0.01	0.005 ± 0.004	0.002 ± 0.001	0.18
Miscellaneous	0.001 ± 0.001	0 ± 0	0 ± 0	0.0005 ± 0.005	0.59
Total	4.52 ± 0.71	3.52 ± 0.22	3.84 ± 0.45	3.80 ± 0.16	0.65

Table 3.4. Individual tree species foliar litter chemistry. Row values with different letters indicate a significant difference among subcatchments ($P < 0.05$). Lime effect P values display overall effect of liming. Mean values are reported ± SE (n = 5 plots).

Tree species	Subcatchment C1	C2	L1	L2	Lime effect (P value)
Beech					
N (%)	1.02 ± 0.03	1.03 ± 0.05	1.03 ± 0.02	1.02 ± 0.04	0.98
C (%)	50.31 ± 0.42 [a]	50.57 ± 0.31 [a]	47.86 ± 0.24 [b]	49.82 ± 0.19 [a]	* < 0.0001
C:N ratio	49.54 ± 1.50	49.74 ± 2.21	46.65 ± 0.90	49.12 ± 1.60	0.29
Ca (%)	0.59 ± 0.05 [a]	0.75 ± 0.05 [ab]	1.06 ± 0.03 [c]	0.87 ± 0.06 [bc]	* < 0.0001
Lignin (%)	35.9 ± 1.6	37.1 ± 2.4	31.0 ± 2.0	31.7 ± 1.7	* 0.02
Red maple					
N (%)	0.76 ± 0.03	0.87 ± 0.06	0.78 ± 0.02	0.86 ± 0.06	0.90
C (%)	50.22 ± 0.23a	50.01 ± 0.32a	48.22 ± 0.05b	49.71 ± 0.23a	* 0.0001
C:N ratio	66.33 ± 2.71	58.83 ± 3.98	62.36 ± 1.71	58.58 ± 3.65	0.51
Ca (%)	0.73 ± 0.03 [a]	1.01 ± 0.09 [ab]	1.23 ± 0.08 [b]	1.09 ± 0.08 [b]	* 0.001
Lignin (%)	20.3 ± 0.7	21.8 ± 2.14	19.9 ± 1.1	20.2 ± 1.5	0.50
Striped maple					
N (%)	0.99 ± 0.08	0.97 ± 0.04	0.92 ± 0.04	0.93 ± 0.02	0.30
C (%)	49.24 ± 0.28a	48.60 ± 0.21a	46.53 ± 0.71ab	48.10 ± 0.39b	0.002
C:N ratio	50.97 ± 4.12	50.65 ± 2.35	51.12 ± 1.86	51.60 ± 1.24	0.84
Ca (%)	1.25 ± 0.07 [a]	1.58 ± 0.04 [ab]	2.50 ± 0.29 [c]	2.21 ± 0.19 [bc]	* 0.0001
Lignin (%)	39.7 ± 2.1	39.9 ± 1.4	31.8 ± 0.3	37.3	* 0.04
Sugar maple					
N (%)	0.76 ± 0.03	0.93 ± 0.10	0.86 ± 0.00	0.80 ± 0.06	0.87
C (%)	49.91 ± 0.28a	48.85 ± 0.29ab	47.97 ± 0.65b	47.83 ± 0.20b	* 0.0005
C:N ratio	65.82 ± 2.75	55.32 ± 5.98	55.73 ± 0.66	60.75 ± 4.50	0.62
Ca (%)	0.52 ± 0.03a	0.96 ± 0.11b	1.53 ± 0.22c	1.65 ± 0.04c	* 0.0001
Lignin (%)	22.2 ± 1.7	21.2	21.7	21.7 ± 1.6	1.0
Yellow birch					
N (%)	1.41 ± 0.06	1.37 ± 0.10	1.25 ± 0.07	1.38 ± 0.06	0.29
C (%)	50.19 ± 0.12 [a]	49.17 ± 0.12 [c]	49.49 ± 0.20 [bc]	49.89 ± 0.12 [ab]	0.96
C:N ratio	35.80 ± 1.53	36.66 ± 2.74	40.26 ± 2.37	36.52 ± 1.47	0.32
Ca (%)	1.15 ± 0.09 [a]	1.33 ± 0.06 [a]	1.83 ± 0.09 [b]	1.51 ± 0.03 [c]	* 0.0001
Lignin (%)	39.5 ± 1.1	32.3 ± 2.1	34.6 ± 0.3	34.1 ± 2.5	0.40

Table 3.5. Total (species combined) annual foliar litter inputs of C, N, and Ca, and Ca and lignin concentrations. Row values with different letters indicate a significant difference among subcatchments ($P < 0.05$). Lime effect P value displays the overall effect of liming. Mean values are reported ± SE (n = 5 plots).

	Subcatchment				Lime effect
Foliar chemistry	C1	C2	L1	L2	(P value)
C (t ha^{-1} yr^{-1})	1.35 ± 0.08	1.36 ± 0.08	1.39 ± 0.19	1.44 ± 0.04	0.60
N (t ha^{-1} yr^{-1})	0.03 ± 0.002	0.03 ± 0.002	0.03 ± 0.004	0.03 ± 0.002	0.12
Ca (t ha^{-1} yr^{-1})	0.02 ± 0.002 [a]	0.02 ± 0.002 [a]	0.04 ± 0.008 [b]	0.04 ± 0.001 [ab]	* 0.001
Ca (%)	0.81 ± 0.02 [a]	1.1 ± 0.04 [b]	1.7 ± 0.1 [c]	1.5 ± 0.04 [c]	* < 0.0001
Lignin (%)	30.7 ± 3.9 [ab]	34.6 ± 4.3 [a]	28.1 ± 3.0 [b]	28.6 ± 3.2 [b]	* 0.01

Table 3.6. Fine root biomass < 2 mm diameter (t C ha^{-1}) in the Oe and Oa forest floor horizons. Row values with different letters indicate significant differences among subcatchments (P < 0.05) and lime effect P values indicate significant responses to liming.

Forest floor horizon	Subcatchment C1	C2	L1	L2	Lime effect (P value)
Oe	0.26 ± 0.04 [a]	0.31 ± 0.06 [a]	0.59 ± 0.05 [b]	0.27 ± 0.04 [a]	* 0.01
Oa	0.22 ± 0.05	0.44 ± 0.05	0.40 ± 0.08	0.45 ± 0.05	0.11

liming on fine root biomass in the Oa horizon; however, there was a trend toward greater biomass in limed soils.

Soil response to liming

Nineteen years after the lime addition, ~48% of the added Ca was present in an exchangeable form within the forest floor and top 40 cm of mineral soil (Table 3.7). Total soil exchangeable Ca stocks were significantly higher in limed soils for all measured depths. The largest stocks occurred in the Oa horizon. Similarly, the largest concentrations of exchangeable Ca were in the forest floor, where both limed subcatchments showed significantly higher concentrations than controls ($P < 0.0001$ for both Oe and Oa; Figure 3.1A). Liming also resulted in significantly higher exchangeable Ca availability within mineral soils, to a depth of 30 cm ($P < 0.01$ for all depths). In response to the liming, the pH of the Oe layer increased significantly from 4.1 to 5.3 ($P < 0.0001$) and in the Oa layer from 3.9 to 4.7 ($P < 0.0001$; Figure 3.1B). In the mineral soils, significantly higher pH was only observed in the 0 - 10 cm increment ($P = 0.05$). Exchangeable magnesium pools did not differ significantly for any studied depth (data not shown).

The forest floor mass was significantly larger in limed soils relative to controls (175 vs. 94 t OM ha^{-1}), resulting in larger forest floor C and N stocks in limed plots (Figure 3.2A and B). This difference in C and N content was driven primarily by greater accumulation of Oa material in the limed subcatchments, which contained 57.5 t C ha^{-1} relative to 23.1 t C ha^{-1} ($P = 0.0002$) in controls and 2.5 vs. 1.1 t N ha^{-1} ($P = 0.0001$). The Oe also contained significantly larger C and N

Table 3.7. Soil exchangeable Ca stocks and estimated percent of added Ca still present in 2007-2008. Percentage calculations assume a Ca application rate of 68.87 kmol Ca ha^{-1} and that the excess exchangeable Ca observed in limed soils relative to controls originated from the lime addition. Row values with different letters indicate significant differences among subcatchments.

Soil depth	Subcatchment				Lime effect
	C1	C2	L1	L2	(P value)
Soil Ca stocks (kmol Ca ha^{-1})					
Oe	1.4 ± 0.3 [a]	0.9 ± 0.3 [a]	6.1 ± 1.6 [b]	4.7 ± 1.0 [b]	* < 0.0001
Oa	1.1 ± 0.5 [a]	1.5 ± 1.0 [a]	19.3 ± 5.2 [b]	20.0 ± 5.0 [b]	* < 0.0001
0 - 10 cm	1.4 ± 0.4 [a]	1.9 ± 0.9 [a]	6.7 ± 2.3 [b]	7.5 ± 3.2 [b]	* 0.0002
10 - 20 cm	0.8 ± 0.2 [a]	1.3 ± 0.6 [ab]	2.6 ± 0.6 [bc]	3.2 ± 0.8 [c]	* 0.0003
20 - 30 cm	0.6 ± 0.2 [a]	0.9 ± 0.3 [a]	1.7 ± 0.4 [ab]	2.5 ± 0.6 [b]	* 0.0002
30 - 40 cm	0.6 ± 0.1 [a]	0.8 ± 0.3 [ab]	1.5 ± 0.4 [bc]	2.0 ± 0.4 [c]	* 0.0002
Percent of added Ca residing in limed soils					
Oe	-	-	7	6	
Oa	-	-	26	27	
0 - 10 cm	-	-	8	8	
10 - 20 cm	-	-	3	3	
20 - 30 cm	-	-	2	2	
30 - 40 cm	-	-	1	2	

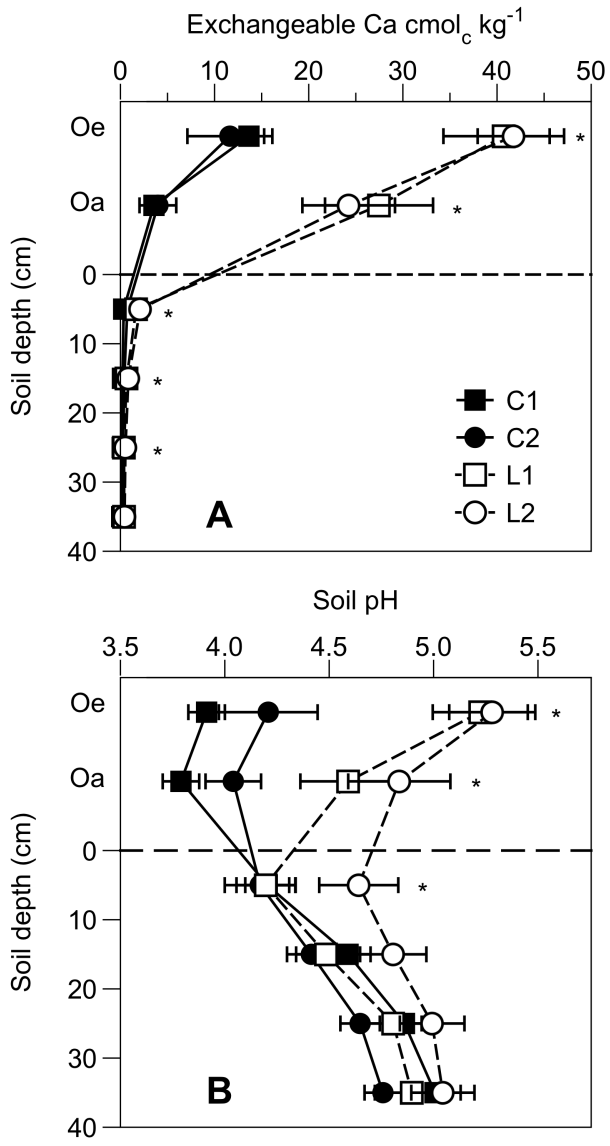

Figure 3.1. Exchangeable Ca concentration (A) and soil pH (B) for all measured forest floor and mineral soil depth increments (Oe, Oa, 0 - 10 cm 10 - 20 cm, 20 - 30 cm, 30 - 40 cm). Significant effects of liming are indicated by * ($P < 0.01$). Error bars indicate ± SE (n = 5 plots).

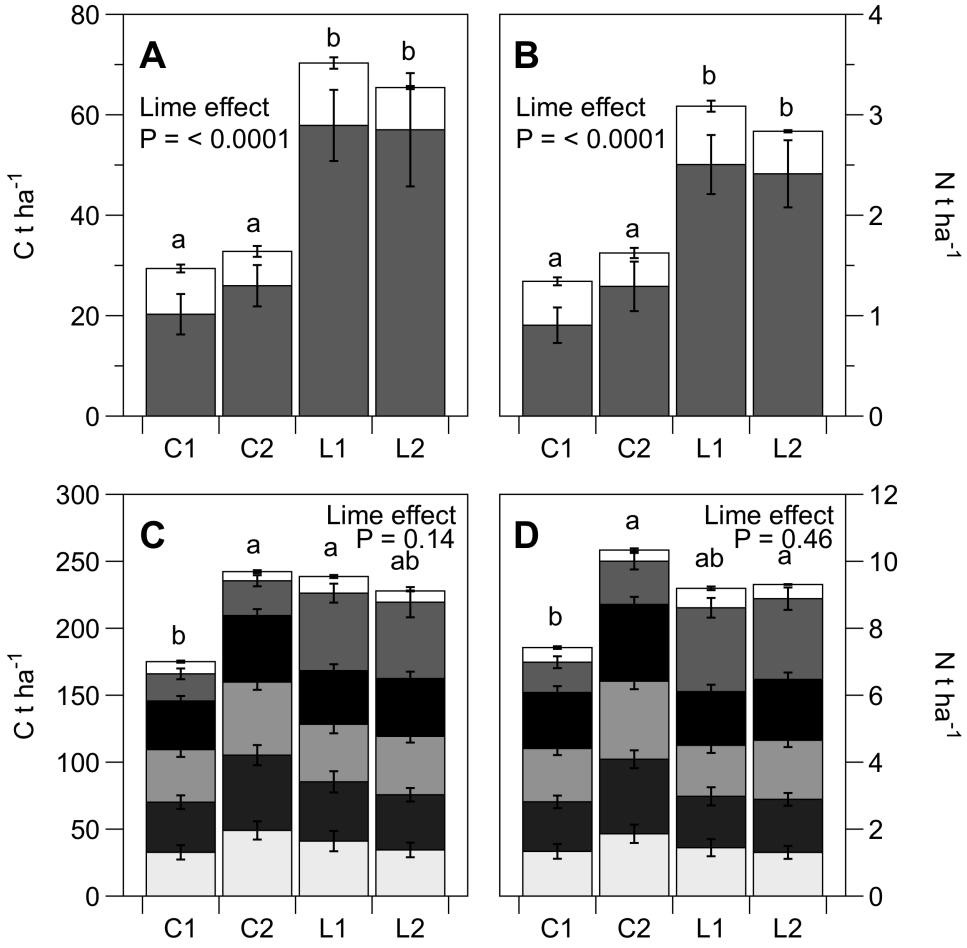

Figure 3.2. Cumulative soil C and N stocks for forest floor (A and B) and combined forest floor and top 40 cm of mineral soil (C and D) displayed with subcatchment mean values for each measured depth increment ± SE (n = 5 plots). Forest floor Oe horizon is displayed in white and Oa in gray in A and B. Mineral soil depth increments (0 - 10 cm 10 - 20 cm, 20 - 30 cm, 30 - 40 cm) are stacked below forest floor in C and D, with the 30 - 40 cm closest to the x-axis. Different letters indicate significant differences in cumulative C and N stocks among subcatchments. Lime effect indicates overall effect of liming on C and N stocks.

stocks in the limed subcatchments, but treatment differences were not as large as those in the Oa (10.4 vs. 8.0 t C ha^{-1}, P = 0.01 and 0.5 vs. 0.4 t N ha^{-1}, P = 0.01). A significantly higher C concentration in the limed Oa horizon was also observed (36 vs. 29%, in limed and control Oa, respectively, P = 0.009). No differences in C concentration were present in the Oe horizon (P = 0.44) or in N concentration for either forest floor horizon (Oe, P = 0.47 and Oa, P = 0.09). Mean forest floor depths from our watershed-wide measurements were 10 cm in control forest floor and 13 cm in limed. Estimated depths in the study plots were 11 cm for controls and 18 cm for limed. These results suggest a similar pattern of increased accumulation in limed soils; however, the relative difference in forest floor depth between limed and control soils was 57% lower with the more comprehensive watershed sampling.

In contrast to the forest floor, effects of liming on mineral soil C and N were less clear. Significant differences among subcatchments were observed for both C and N concentrations and stocks, for all depth increments ($P < 0.05$). Overall liming effects indicate significantly larger cumulative C and N stocks in control soils for 0 - 40 cm depth (P = 0.03 and 0.0007 for C and N, respectively). This finding was driven primarily by significantly higher C and N concentrations in the mineral soils within the C2 subcatchment, relative to all other subcatchments. Therefore, it is unclear if this is a liming effect or due to inherent mineral soil heterogeneity. As a result of this difference in mineral soil C and N, the cumulative stocks of C and N in the forest floor and upper 40 cm of mineral soil did not differ significantly between limed and control soils (P = 0.14 and 0.46 for C and N, respectively). Instead, the total forest floor and mineral soil stocks of C and N in the C2 were more similar to the total stocks in the limed subcatchments while the C1 subcatchment values were lower (Figure 3.2C and D).

The soil C:N ratio increased with soil depth from a mean value of 21 in the Oe horizon to 27 in the 30 - 40 cm mineral soil depth increment (Figure 3.3). Liming resulted in a significantly larger C:N ratio in the Oa forest floor horizon and in the mineral soil depth increments 0 - 10 cm, 10 - 20 cm, and 20 - 30 cm ($P < 0.05$). These differences were driven primarily by a larger C:N ratio within the L1 limed subcatchment.

Soil basal respiration was significantly lower in the forest floor of limed soils relative to controls, particularly for the Oa horizon ($P = 0.04$ and < 0.0001 for Oe and Oa, respectively; Figure 3.4A and B). Soil basal respiration was 17% lower in the Oe horizon of limed soils and reduced by 43% in the Oa layer. The ^{13}C values of C respired as CO_2 did not differ significantly between limed and control forest floor material for either horizon ($\delta^{13}C = -25.6$, $P = 0.10$ for Oe and $\delta^{13}C = -24.1$, $P = 0.30$ for Oa), suggesting that abiotic CO_2 production caused by dissolution of any remaining lime pellets did not influence observed values.

Net N mineralization expressed on a mg N kg^{-1} soil basis indicated significantly lower rates in the limed soils for both forest floor horizons ($P = 0.0003$ and 0.0032 for Oe and Oa, respectively; Figure 3.5A and C). No effect of liming on N mineralization in the top 0 - 10 cm of mineral soil was observed ($P = 0.74$; Figure 3.5E). Net nitrification was significantly higher in the limed soils in the Oe horizon ($P < 0.0001$; Figure 3.5B), while no differences were evident in the Oa ($P = 0.95$; Figure 3.5D) or upper mineral soils ($P = 0.60$; Figure 3.5F). Considering these N cycling measurements on an areal basis (kg N ha^{-1}) reveals a slightly different pattern. Limed Oa material showed significantly lower net N mineralization rates than controls (0.07 vs. 0.11 kg N ha^{-1} day^{-1}, $P = 0.05$) while no significant differences were observed in the Oe and 0 - 10 cm mineral soil depths ($P = 0.06$ and 0.81, respectively). Areal-based net nitrification rates were

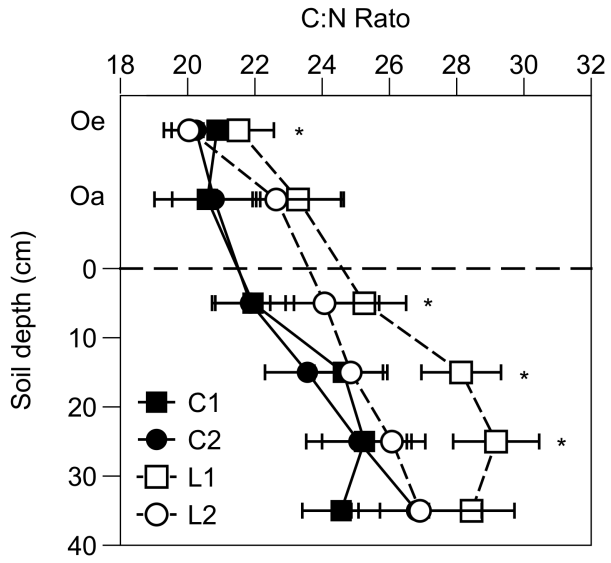

Figure 3.3. Mean forest floor and mineral soil C:N ratio for each subcatchment ± SE (n = 5 plots). * indicates significant differences among subcatchments ($P < 0.05$) and is detailed in the text.

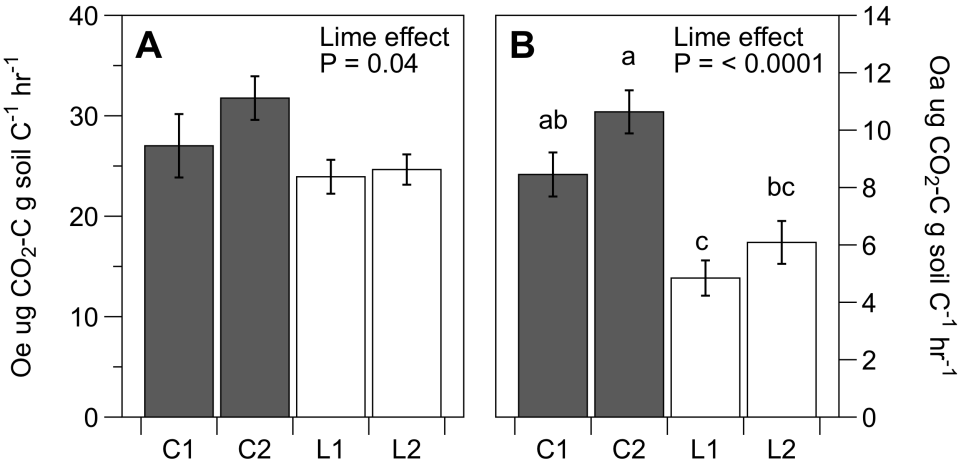

Figure 3.4. Soil basal respiration for Oe (A) and Oa (B) forest floor horizons. Mean values represent plot means within each subcatchment for the two sampling dates ± SE. Different letters indicate significant differences among subcatchments. Lime effect indicates overall effect of liming.

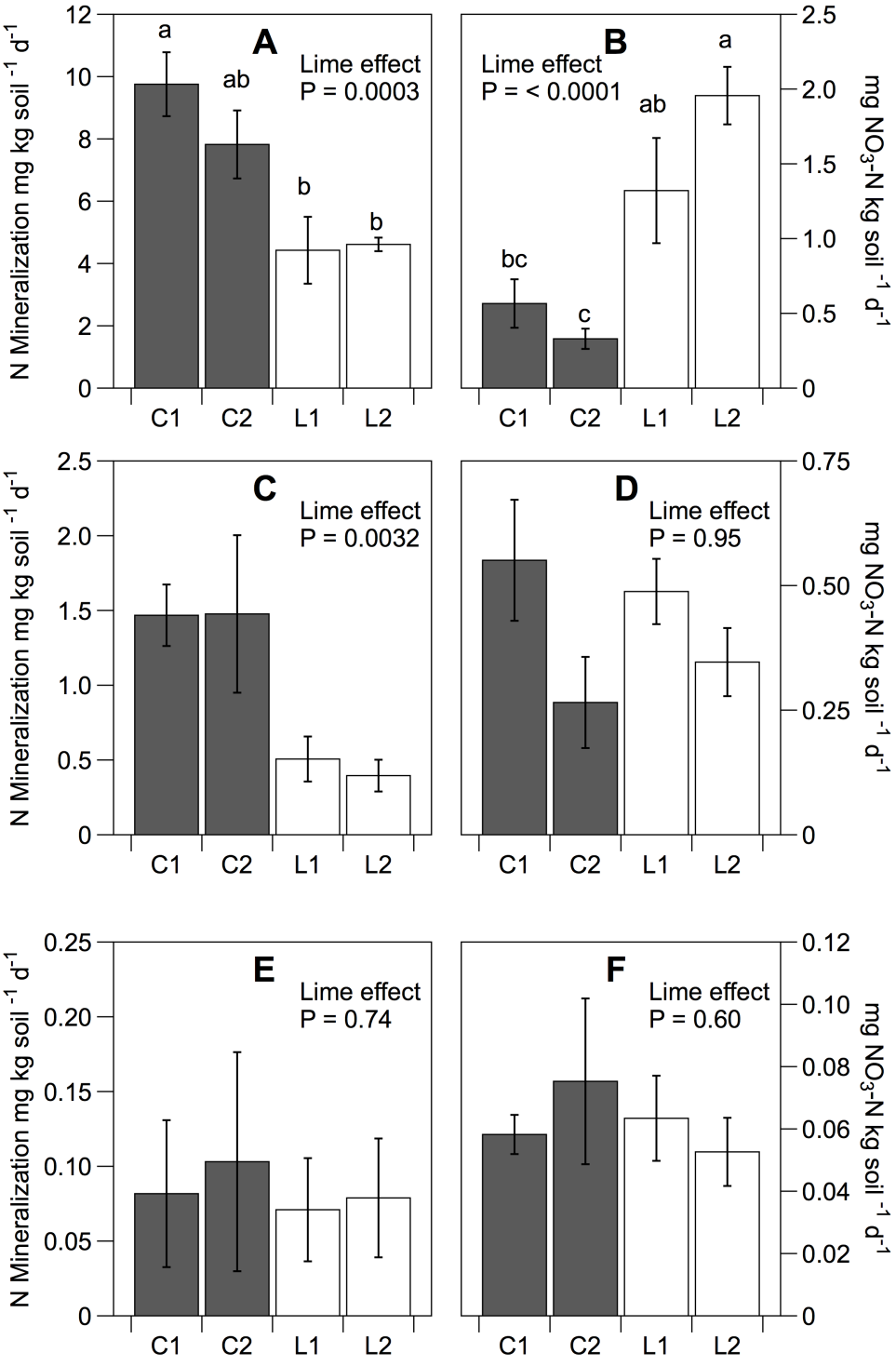

Figure 3.5. Net N mineralization for Oe (A), Oa (C), and 0 - 10 cm mineral soil (E) and nitrification for the same depths (B, D, F) displayed as mean ± SE for each subcatchment. Different letters indicate significant differences among studied subcatchments ($P < 0.05$). Lime effect indicates overall effect of liming.

significantly higher in both Oe and Oa forest floor horizons in the limed soils (P = 0.0004 and 0.03, respectively).

DISCUSSION

Liming effects on forest floor C and N cycling and stocks

Liming in the Woods Lake Watershed showed large and unexpected effects on C and N cycling 20 years after the lime addition. Perhaps most dramatically, the forest floor in the limed subcatchments was much larger than in the controls, resulting in almost twice the C and N storage in the organic horizons. We had hypothesized that the increase in pH associated with liming would stimulate decomposition and reduce OM accumulation in the forest floor of limed subcatchments, as has been shown in many other studies (Zelles et al. 1987, Shah et al. 1990, Valeur and Nilsson 1993, Andersson and Valeur 1994, Baath and Arnebrant 1994, Priha and Smolander 1994, Smolander et al. 1994, Andersson and Nilsson 2001). These C mineralization studies typically measured respiration immediately following Ca addition, however, which may only reveal a short-term response. Others have found a decline in respiration after the initial enhancement, occurring days to weeks after addition (Persson et al. 1989, Persson et al. 1990, Illmer and Schinner 1991, Neale et al. 1997, Groffman et al. 2006). Previous *in situ* measurements of soil respiration at Woods Lake within the first year after liming showed a trend toward higher CO_2 efflux in control relative to limed soil in the peak of summer, but this pattern was not significant (Yavitt et al. 1995). Enhanced forest floor accumulation with liming has been observed previously in conifer forests in Finland and was believed to be caused by increased OM inputs from ground vegetation, although they did not quantify these inputs (Derome 1990). Others report either no change (Lofgren et al. 2009) or large reductions in forest floor mass and C stocks in response to liming 7-40 years after lime application (Kreutzer 1995, Persson et al.

1995). The reasons for these differential responses remain unclear. At Woods Lake, it appears that a decrease in decomposition rate is the primary driver of forest floor accumulation, rather than an increase in litter or root inputs.

The large reduction in soil basal respiration that we observed suggests that the lime has altered the relationship between the microbial community and the organic matter it mineralizes. There are many ways in which liming could influence soil-microbe interactions, including: 1) changes in the microbial community, 2) altered recalcitrance of the OM produced, or 3) physical stabilization of OM. It is possible that the microbial community in the limed plots has shifted from being more fungal to bacterial dominated, as has been shown in other studies (Ivarson 1977, Baath and Arnebrant 1994, Andersson and Nilsson 2001). A new community may be unable to utilize the C substrate as effectively, either through a change in microbial population size, enzyme activity, or efficiency.

Alternatively, decomposition rates might decrease if plants respond to liming by producing more recalcitrant litter. Plant physiological research has shown that higher Ca availability can increase the lignin concentration in cell walls of tree seedling shoots (Eklund and Eliasson 1990). We hypothesized that increased Ca availability could enhance lignin production, leading to more recalcitrant litter inputs in limed plots. Our findings indicated the opposite however, that leaf litter lignin concentration was larger in controls than in limed plots, and that the lignin:N ratio in litter did not differ by liming treatment, suggesting that a shift in litter lignin concentration is not a driver of reduced decomposition rate. It is possible that liming could have increased quantities of other recalcitrant compounds that we did not measure.

Another possible explanation for the observed increase in Oa mass is that the OM has become physically stabilized via Ca-OM bridging. This mechanism is well studied in laboratory

experiments using pure minerals and in agricultural soils (Oades 1988, Muneer and Oades 1989, Mikutta et al. 2007) and has been suggested as a factor influencing soil C and N accumulation in forest soils with neutral pH (5-8) (Paul et al. 2003, Morris et al. 2007) and in tundra ecosystems (pH 6-7) (Hobbie et al. 2002). Additionally, liming has been shown to enhance initial soil C losses, but over time lead to greater C accumulation in the limed soils relative to controls in an agricultural soil (Chan and Heenan 1999). Chan et al. suggested this was due to increased aggregate stability and greater Ca-OM bridging. This initial enhancement in C loss followed by improved OM stability could be the result of increased pH leading to solubilization of more labile C, which then leaves the remaining C pool relatively enriched in more recalcitrant C compounds. In acidic forest soils, Al is typically the dominant binding element (Oades 1988), and therefore little research has been done to explore Ca-OM bridging. In managed forests that are limed however, this may be a plausible mechanism to enhance soil C and N stocks. There are studies indicating that Ca-OM complexation can occur in the forest floor (Kalbitz et al. 2000) and we suggest that the increased pH and exchangeable Ca concentrations in the forest floor of limed plots provides an environment in which decadal-scale Ca-OM complexation could occur, thereby reducing microbial access to OM and reducing decomposition.

Forest floor net N mineralization rates were also reduced by liming in both the Oe and Oa horizons. Net nitrification was elevated in limed soils within these horizons, suggesting greater activity of nitrifying microbes. These results are similar to those reported by Simmons et al. (1996), who found reduced N mineralization and enhanced nitrification in response to liming at Woods Lake two years after the lime addition. Studies at other forested sites have also shown suppression of N mineralization with added Ca (Persson et al. 1990, Persson et al. 1995, Groffman et al. 2006) and higher rates of nitrification (De Boer et al. 1993, Andersson and

Valeur 1994, Persson et al. 1995, Smolander et al. 1995, Neale et al. 1997, Ste-Marie and Pare 1999, Clough et al. 2004, Groffman et al. 2006). The pH was most elevated in the Oe forest floor horizon and increased pH has often been linked with increased rates of nitrification (De Boer et al. 1993, Persson et al. 1995, Smolander et al. 1995, Neale et al. 1997, Ste-Marie and Pare 1999).

Estimated forest floor C budget

The forest floor C stock in limed plots was approximately 37 t ha^{-1} greater than that in controls. To explore whether our observed treatment effects on C inputs and losses could quantitatively account for this large difference, we constructed a net C balance using our empirical data and literature values (Table 3.8). Inputs of foliar and non-foliar aboveground litter were calculated separately to reflect the higher input of foliar litter in limed plots and lower input of non-foliar litter (although neither showed a significant liming effect). We assumed that all non-foliar litter contained 50% C. Together, these aboveground inputs accounted for an increase of 0.12 t C ha^{-1} yr^{-1} in the limed forest floor relative to control, or 2.4 t C ha^{-1} in the 20-year period since liming. Fine root C stocks were 0.24 t C ha^{-1} larger in limed soils. Using a turnover rate of 30% (Tierney and Fahey 2002) and an assumption that roots contained 50% C, we estimated enhanced root inputs of 0.07 t C ha^{-1} yr^{-1} due to liming, or 1.4 t C ha^{-1} since 1989.

Soil basal respiration was significantly lower in limed plots relative to controls. We assumed a heterotrophic respiration rate of 2.5 t C ha^{-1} yr^{-1} for forest floor OM; a value calculated for a similar northern hardwood forest at Hubbard, NH by Fahey et al. (2005). Briefly, Fahey et al. inserted a plate between the forest floor and mineral soils and repeatedly measured *in situ* soil respiration. The annual heterotrophic respiration rate was estimated using this

Table 3.8. Estimated annual and 20-year effects of liming on C accumulation in measured input and loss pathways.

Source of C flux	Increase in C stocks in limed soils (t C ha^{-1} yr^{-1})	20-year enhancement in C stocks due to liming (t C ha^{-1})
Foliar litter [nsd]	0.32	6.4
Non-foliar litter [nsd]	-.20	-4.0
< 2mm roots *	0.07	1.4
Heterotrophic respiration *	0.95	19
Observed increase in forest floor C stocks	1.85	37
Enhanced C retention in measured pools	1.14	22.8
C unaccounted for in measured pools		14.2

empirical data, measurements of fine root respiration, and a univariate exponential model which included soil temperature. We used the heterotrophic respiration rate of 2.5 t C ha^{-1} yr^{-1} to estimate the enhanced accumulation of C resulting from reduced respiration losses in limed forest floor. We estimated reductions in C loss separately for the Oe and Oa forest floor horizons because of the large difference in their contribution to the forest floor C stocks. Across all studied plots (treatment and control), approximately 19% of forest floor C stock was in the Oe horizon and 81% was in the Oa. Assuming the heterotrophic respiration is proportional to C stocks in both horizons, approximately 0.47 t C ha^{-1} $yr^{-1}$was respired from the Oe and 2.01 t C ha^{-1} yr^{-1} from the Oa in control soils. Applying our measured 17% suppression of soil basal respiration by lime in the Oe resulted in additional accumulation of 0.08 t C ha^{-1} yr^{-1} in limed soils and the 43% reduction in the Oa resulted in 0.87 t C ha^{-1} greater C retention. Together, this suppression of respiration might account for an increase of 0.95 t C ha^{-1} yr^{-1} in limed soils, or approximately 19 t C ha^{-1} since lime addition.

Combining all C inputs and losses, we estimate that liming could have enhanced forest floor C stocks by ~22.8 t C ha^{-1}. This leaves 14.2 t C ha^{-1} of our observed difference unaccounted for, but all terms in this simple budget are uncertain. For instance, the respiration rate of Oa material is typically lower than that of Oe, indicating that we probably overestimated the increased accumulation of Oa material due to liming. Measurements taken across the entire watershed indicated that the relative difference in forest floor depth between limed and control soils was 57% smaller what we observed in our 20 study plots. Reducing our 37 t C ha^{-1} measured stock difference by 57% yields an expected net enhanced forest floor accumulation due to liming of 15.9 t C ha^{-1}, which is greater than our estimate of enhanced retention of 22.8 t C ha^{-1}.

Additional sources of uncertainty in the C budget include the possibility of a transient response to liming and inherent site differences. Liming may have stimulated aboveground and/or root C inputs or reduced basal respiration more strongly immediately following the liming. The small differences we currently observe in inputs may be the residual effects of a much larger transient response. Pre-existing site heterogeneity could have also influenced observed patterns in forest floor. Unfortunately, there is limited pre-treatment data on forest floor nutrient stocks or mass from all our studied subcatchments. In each of the limed subcatchments, 6 soil pits were excavated prior to liming (Blette and Newton 1996). One control subcatchment had 3 pits, however this was a control subcatchment that was not used in our study because it was harvested in recent years. Blette et al. report data only on soil base cations and acidity and give no indication of differences in the forest floor. Simmons et al. (1996) utilized both limed subcatchment and the C2 control subcatchment for his forest floor N cycling research. He reports mean forest floor thickness data and gives no indication of differences among the subcatchments. Plot selection may have also influenced our findings. As discussed above, forest floor depth measurements taken across the entire watershed indicate that there may be a smaller relative difference in forest floor depth between limed and control subcatchments than we observed in our 20 study plots.

Although our plot C and N stock data for limed soils may overestimate watershed values, the pattern of enhanced C and N accumulation with liming is well supported by our data. Both limed subcatchments show similar relative increases in C and N accumulation compared to both control subcatchments. This is in contrast to the mineral soil C and N pools, which were more variable. Watershed-scale forest floor depth sampling also showed a pattern of deeper forest floor in limed subcatchments relative to controls. Finally, our basal soil respiration

measurements show a strong suppression of CO_2 efflux, indicating that mineralization of available C has been reduced in limed soils. Our C balance estimates suggest that this can account for much of the observed enhanced C accumulation in limed forest floor.

Forest floor N

The additional 1.5 t N ha^{-1} observed in limed forest floor is also difficult to reconcile. Reducing the net difference in N accumulation to account for differences in forest floor depth results in an estimated addition 0.6 t N ha^{-1} in limed forest floor. Similar to C, this treatment difference must stem from either enhanced N inputs or reduced losses from limed forest floor. Total foliar N inputs did not differ between treatment and controls. Slightly higher fine root biomass observed in limed soils also seems unlikely to account for the observed difference. It is possible that the trees may have acquired N from deeper mineral soils and then deposited it as litter in the forest floor. We did not see increased N concentrations in foliar litter, but it is possible that the roots may have increased in N concentrations, a soil pool that we did not quantify. It may also be possible that liming increased N fixation in the forest floor, but this process is not typically observed in temperate forests (Davidson 2008) and seems an unlikely cause of the large N stocks at our study site.

Smaller losses of N from limed forest floors could contribute to the pattern we observed. Net N mineralization was reduced by 31% in Oe and 40% in Oa horizons in limed plots relative to controls. Using an annual net N mineralization rate of 40.1 kg N ha^{-1} yr^{-1} calculated for a nearby Adirondack forest (Ohrui et al. 1999), we estimated that ~15.5 kg N ha^{-1} yr^{-1} of additional N could accumulate as a result of the observed suppression in forest floor N mineralization. This

accounts for 0.31 t N ha^{-1} over the 20-year period since liming and leaves approximately half of the estimated 0.6 t N ha^{-1} forest floor stocks unaccounted for.

Tree response to lime addition

We had expected to see a positive tree growth response to liming, but no response was evident. Previous Ca addition studies have reported enhanced growth (Bakker et al. 1999b, Kakei and Clifford 2002, Moore and Ouimet 2006, Huggett et al. 2007), no response (Derome 1990, Huber et al. 2004), or declines (Derome et al. 1986). Long et al. (1997) found that American beech, a dominant species at our site, did not respond to liming. Also, it has been ~100 years since this forest was harvested and therefore the annual woody biomass accumulation is likely low (Odum 1969) and could contribute to the lack of response to added Ca. The net decline in biomass since liming was driven by the high mortality rate of American beech, which is likely the result of beech bark disease in this region (Latty et al. 2003).

There was a trend towards greater annual foliar litter production in limed plots, but this difference was not significant. It is possible that litter inputs were more elevated after the lime addition and we measured the late stages of this enhancement. Very few Ca addition studies report litter responses. Huber et al. (2004) reported no response in a 77-year old, thinned Norway spruce plantation 2-5 and 9-15 years after liming. Although beyond the scope of our study, tree ring analysis might have revealed whether there was a growth enhancement immediately following the Ca addition that has diminished over time.

We also expected that the enhanced Ca and forest floor pH might stimulate fine root growth or shift root allocation toward surface horizons. Although an overall increase in root biomass in the Oe was observed, this pattern was driven by much greater biomass in the L1

subcatchment relative to all other subcatchments. Some studies have shown increased root production and mycorrhizal infection (Hahn and Marschner 1998, Nowotny et al. 1998, Bakker et al. 1999a), but others have found little or mixed responses to liming (Andersson and Soderstrom 1995, Qian et al. 1998).

Liming studies and relevance to forest recovery from acidification

Among published forest liming studies, the application rate of 2.76 t Ca ha^{-1} at Woods Lake is relatively high. This was well beyond a replenishment of Ca lost as a result of acid deposition (estimated to be ~0.85 t Ca ha^{-1} in NH; Groffman et al. 2006) and therefore may be viewed more as a Ca fertilization experiment than as assisted recovery to pre-acid deposition conditions. In regions where declines in acid deposition have been documented, we may not expect to see similar C and N responses without a large pulse of added Ca and shift in pH generated by liming.

Forest C and N responses to natural de-acidification contrast with the results to our study. In the Czech Republic, Oulehle et al. (2011) measured significant declines in sulfur (S) deposition and soil water sulfate concentrations in recent decades, with concurrent declines in C and N stocks in the forest floor Oa horizon averaging 1.16 t C ha^{-1} yr^{-1} and 0.04 t N ha^{-1} yr^{-1}. They attributed these changes to increased decomposition and loss of C as CO_2, greater N uptake by trees, and increased translocation of N into the mineral soil. Forest floor pH did not change over this time. This indicates that forest floor decomposition may be affected more strongly by soil S concentrations (or another factor directly related to soil S) than by an increase in soil pH. In our study, the large dose of lime may have pushed the pH too far in the opposite direction, thereby reducing microbial activity. Also, the large increase in exchangeable Ca concentration

may have affected the microbes, or led to increased OM stabilization and reduced microbial access. Interestingly, rates of C and N loss in the Oa horizon observed by Oulehle et al. are similar in magnitude to our estimated rates of Oa accumulation (1.8 t C ha^{-1} yr^{-1} and 0.07 t N ha^{-1} yr^{-1}).

Conclusions

Our results highlight the importance of the coupled interactions among C, N, and Ca cycles and suggest that liming can have large and sometimes surprising effects on ecosystem C and N balance. While these findings are in concert with some Ca addition studies, we also observed some dramatic differences. Most strikingly, the large increase in forest floor C and N stocks and the suppression of basal soil respiration differ from most published Ca responses. Additional research is needed to identify the primary drivers of altered decomposition rates in response to liming in mixed northern hardwood forests. This work should include study of microbial community dynamics, OM recalcitrance, and physical stabilization. The northeastern U.S. has experienced high acid deposition rates, declines in soil pH and exchangeable Ca availability, which may have long-term, detrimental effects on C sequestration and storage, and ecosystem N retention. Refining our understanding of the mechanisms driving changes in soil OM dynamics and the specific role of Ca is essential to understanding C and N fluxes in acid-impacted forest ecosystems.

APPENDIX 3A

The detailed transect and plot information provided below is a combination of information obtained from Peter Smallidge (personal communication) and collected during this study.

Notes on transect locations

Transect 2-1: The first 2 plots on this transect were logged between 1989 and 2009. The first intact plot is 2103, which is located upslope, SW of the stream draining the beaver pond. Plot 2103 runs along the edge of the state-private land boundary (trees marked with yellow paint). This transect is 525 m long, with a bearing of 310^{o}.

Transect 2-2: Transect starts approximately 20 m N of the beaver dam at the end of the beaver meadow. This transect is 450 m in length and runs at a bearing of 350^{o}.

Transect 3-1: This transect starts approximately 75 m inland from the lake edge and has no easy landmarks to identify it. Use the GPS coordinates given for studied plots on this transect to find it. The transect runs 585 m at a bearing of 320^{o}.

Transect 3-2: Transect starts at the same location as 3-1. Use given GPS coordinates to locate it. Transect is 300 m long, on a bearing of 10^{o}.

Subcatchment 4 transects: All transects in this subcatchment begin from a gray post located in a marshy area at the far end of the lake. The post is difficult to find, but located at N 43.87480, W 74.94631.

Transect 4-2: Transect has a length of 605 m, at a bearing of 60^{o}.

Transect 4-3: Transect is 685 m in length, at a bearing of 80^{o}

Transect 4-4: Transect is 455 m long, running at a bearing of 110^{o}.

Transect 5-1: This transect starts where the state-private land boundary meets the lake. Tagged trees may be visible from the trail. The transect is 300 m long, on a bearing of 150^{o}. This is the only transect in this subcatchment.

Additional transects that were not sampled for this study:

Transect 3-3: Transect begins at water's edge, with no easily identifiable markers. The first plot (3301) is located at N 43.87497, W 74.94856. Transect is 585 m long and runs at a bearing of 30^{o}.

Transect 4-1: Among the transects in subcatchment 4, this one is located closest to subcatchment 3, at the opposite end of the lake from the cabin. Transect is 765 m in length, on a bearing of 40^{o}. The first ~150 m of this transect passes through a sedge/low shrub wetland.

Table 3.1A. Basic plot information and locations.

Treatment	Subcatchment Number	Transect	Subcatchment notation used	Plot	Slope	Aspect	GPS Coordinates
Control	3	3-1	C1	3102	19	147	N 43.87520, W 74.95200
Control	3	3-1	C1	3103	29	139	N 43.87545, W 74.95255
Control	3	3-1	C1	3107	2	91	N 43.87654, W 74.95440
Control	3	3-2	C1	3202	23	171	N 43.87557, W 74.95079
Control	3	3-2	C1	3204	45	140	N 43.87628, W 74.95097
Control	5	5-1	C2	5101	17	348	N 43.87212, W 74.94859
Control	5	5-1	C2	5102	6	328	N 43.87178, W 74.94808
Control	5	5-1	C2	5103	13	336	N 43.87158, W 74.94769
Control	5	5-1	C2	5104	19	8	N 43.87110, W 74.94708
Control	5	5-1	C2	5105	1	351	N 43.87085, W 74.94675
Limed	2	2-1	L1	2103	25	39	N 43.87179, W 74.95580
Limed	2	2-1	L1	2107	5	111	N 43.87276, W 74.95792
Limed	2	2-1	L1	2109	13	96	N 43.87317, W 74.95918
Limed	2	2-2	L1	2201	37	240	N 43.87284, W 74.95566
Limed	2	2-2	L1	2206	20	248	N 43.87508, W 74.95674
Limed	2	4-2	L2	4205	13	300	N 43.87545, W 74.94514
Limed	2	4-2	L2	4206	14	320	N 43.87573, W 74.94453
Limed	2	4-3	L2	4304	12	288	N 43.87446, W 74.94536
Limed	2	4-3	L2	4305	12	296	N 43.87483, W 74.94435
Limed	2	4-4	L2	4403	21	340	N 43.87378, W 74.94577

Table 3.2A. Live tree biomass in 2009 (t OM ha^{-1}) by plot and species.

		Tree species						
Subcatchment	Plot	Beech	Red maple	Red spruce	Striped maple	Sugar maple	Yellow birch	Total
C1	3102	35.9	69.2	13.3	0.9	49.4	63.4	232.2
C1	3103	42.7	11.5	8.3	0.0	154.7	12.6	229.9
C1	3107	75.9	0.0	32.2	20.9	3.3	0.0	132.2
C1	3202	19.1	96.2	0.0	1.4	20.1	5.4	142.1
C1	3204	9.6	92.1	0.0	7.3	0.0	67.2	176.2
C2	5101	25.0	144.1	0.0	0.0	0.0	0.0	169.1
C2	5102	12.1	20.0	3.0	33.5	16.2	0.9	85.8
C2	5103	110.3	32.7	5.6	1.8	0.0	13.3	163.7
C2	5104	116.4	0.0	0.0	0.0	0.0	6.1	122.4
C2	5105	147.9	0.0	0.8	3.6	0.0	0.0	152.3
L1	2103	36.6	19.0	0.0	4.9	0.0	378.5	439.1
L1	2107	53.2	21.8	29.3	0.0	0.0	24.1	128.4
L1	2109	20.5	19.4	5.0	14.1	0.0	167.4	226.4
L1	2201	25.5	65.6	13.9	0.0	0.0	4.5	109.5
L1	2206	21.7	57.2	13.4	0.0	6.9	73.6	172.8
L2	4205	12.4	72.9	0.0	3.2	0.0	74.9	163.3
L2	4206	38.0	46.1	7.1	9.1	0.0	6.0	106.3
L2	4304	30.4	70.5	0.0	1.2	31.6	0.0	133.7
L2	4305	34.9	1.9	5.3	4.3	18.9	36.9	102.2
L2	4403	9.2	8.1	35.3	1.7	21.1	26.9	102.2

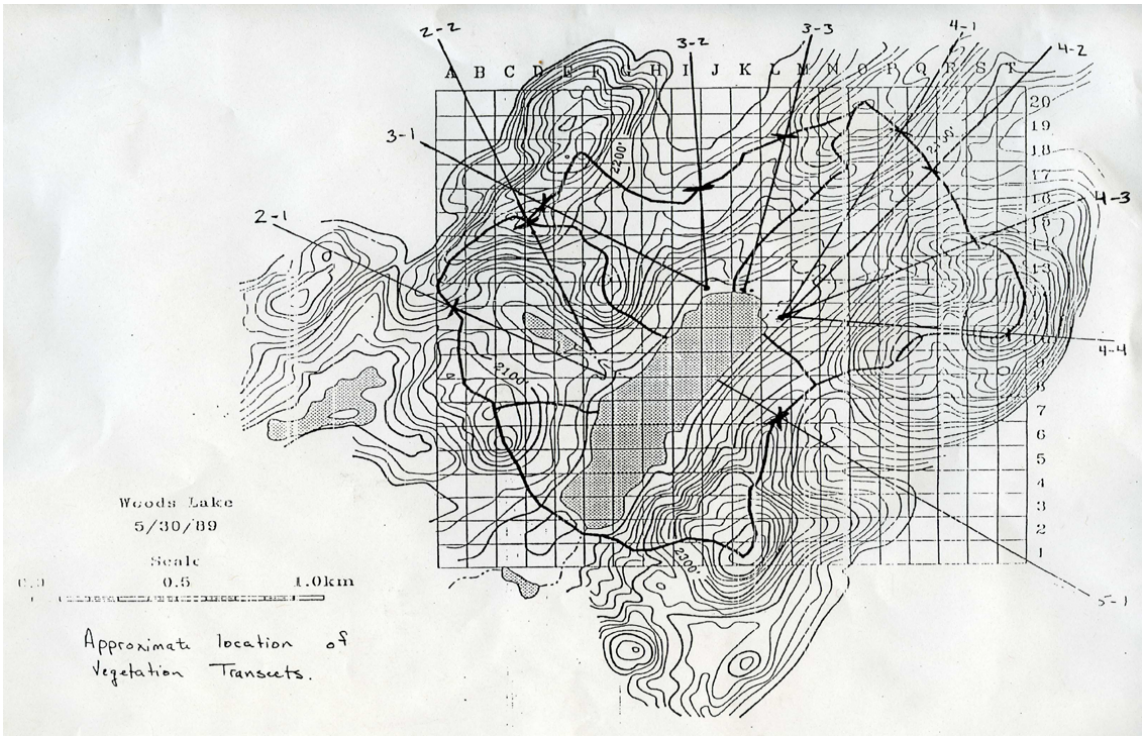

Figure 3.1A. Map of approximate transect locations (from Peter Smallidge).

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